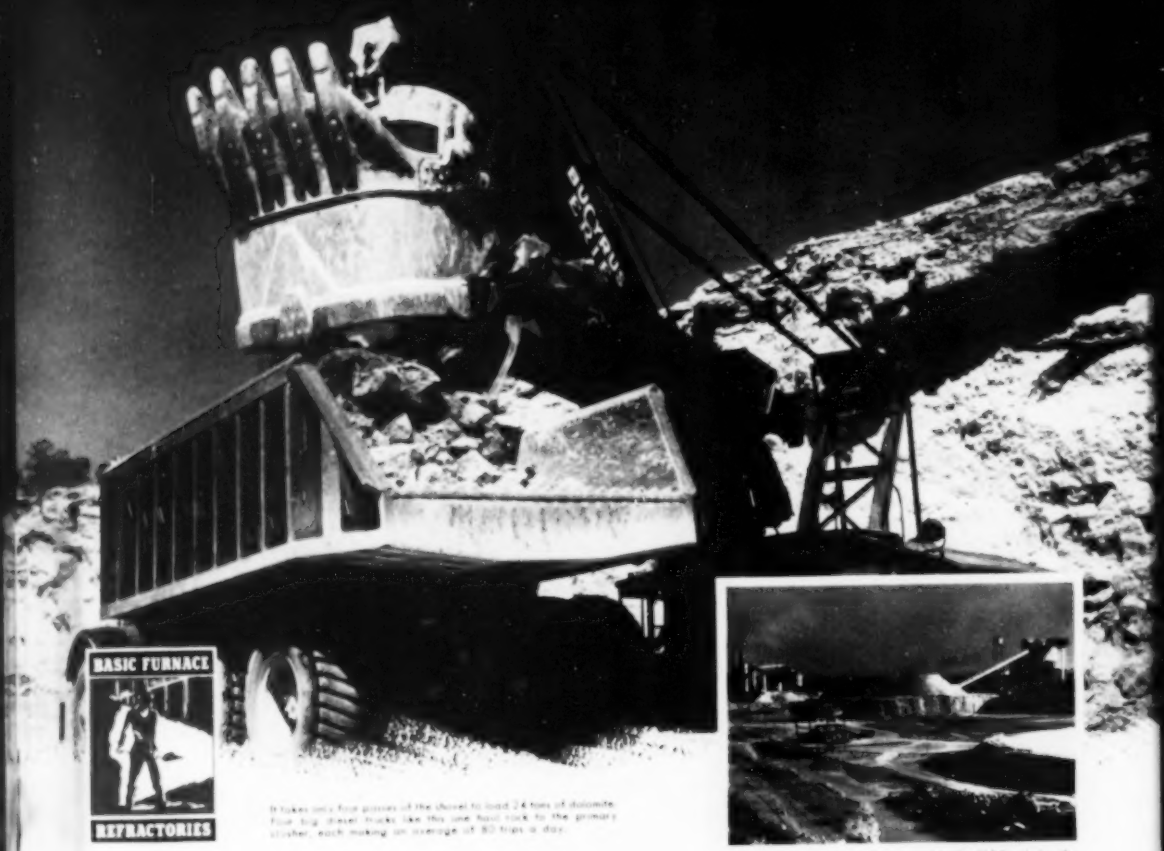
MAY, 1952

Journal of METALS

May JOURNAL OF METALS Highlights:

"Production at Garfield Smelter" - p. 456
"Open Hearth Rebuild Program" - p. 465
"Chromium Carbide in Stainless Steel" - p. 469



BASIC FURNACE REFRACTORIES

It takes only four passes of the shovel to load 24 tons of dolomite. Five big diesel trucks like this one haul rock to the primary crusher, each making an average of 30 trips a day.

This is the ore production line—primary crusher 160 feet below the quarry floor; belt conveyor to 30,000-ton surge pile; belt conveyor to preparation plant housing secondary crushers and classifiers.

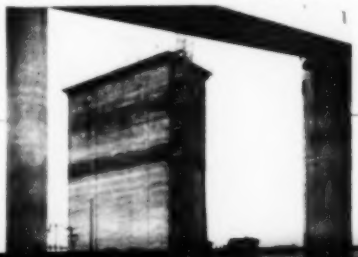
Rock garden for steel plants

Steel plants live by the cultivation of this rock garden. For from this bed comes dolomite for Magnefer, Syndolag and other basic refractories used in the production of open hearth and electric furnace steel.

To keep pace with the expansion of the steel industry, we are enlarging our facilities for quarrying and preparation of ore, as well as for dead burning refractories. Happily, our reserves of this unusually pure dolomite at Maple Grove are sufficiently extensive to take care of the industry's needs for basic furnace refractories for an estimated 100 years.

One of the ore classifiers sizing dolomite for Magnefer. Wet screening removes all fines and undersized particles, thus insuring uniformity of grain size in the finished refractory.

Sized raw dolomite, ready for dead burning, is stored in huge silos at the feed ends of kilns. This new silo, 122 feet high, largest of its kind, will feed two new rotary kilns now being installed.



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Journal of **METALS**

VOL. 4, NO. 5 MAY, 1952

Published to provide a continuing, authoritative, and up-to-date record of technological, engineering, and economic progress in all branches of the metals industry by the Metals Branch American Institute of Mining and Metallurgical Engineers, Inc. 29 West 39th Street, New York 18

COVER

A 3x8 ft Marcy Mill is shown in operation in closed circuit with a 30-in. Akins classifier grinding manganese ore from Artillery Peak, Ariz., at the Bureau of Mines station at Boulder City, Nev., where economical methods of producing an acceptable manganese product from low grade domestic ores are being sought.

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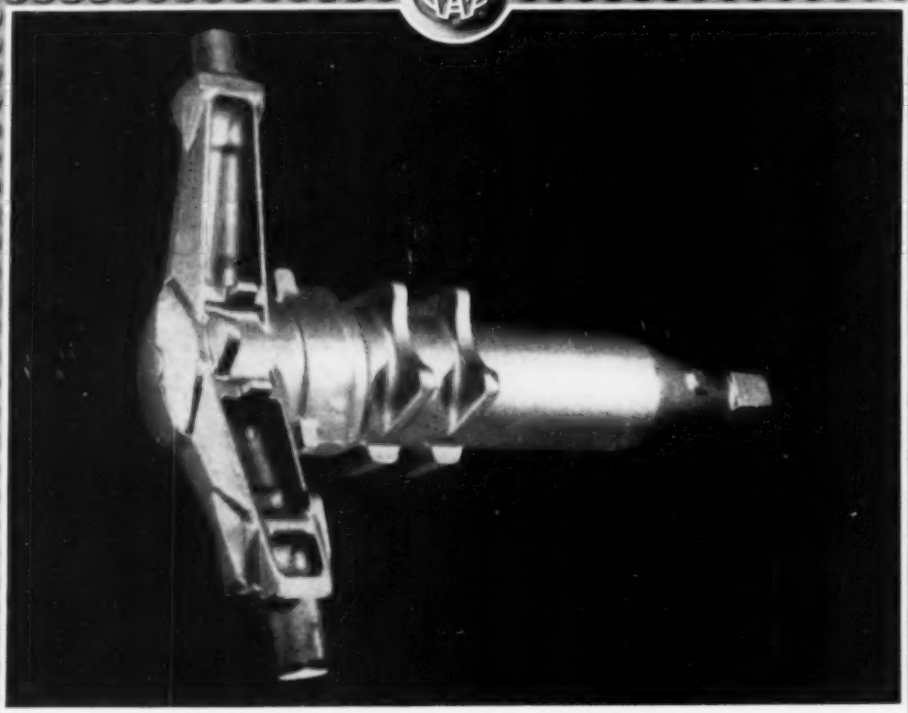

Forgings for the aircraft industry today demand the utmost in engineering and production techniques and in scientific laboratory control. This massive complicated landing gear component, weighing over 400 pounds, is typical of Wyman-Gordon's forging contribution to the ever-growing progress in aircraft design. In crankshafts for the automotive industry and in all types of aircraft forgings, steel and light alloy, Wyman-Gordon has pioneered in the development of forging "know-how"—there is no substitute for Wyman-Gordon experience.

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MEET THE AUTHORS

AUGUSTUS B KINZEL

Augustus B. Kinzel (p. 469) was born in New York City, graduated from Columbia University in 1919 (A.B.); from Massachusetts Institute of Technology, 1921 (B.S. General Engineering); and University of Nancy, France, 1922 (D.Met. Ing.), where he also received the degree of Doctor of Science. In 1922 he joined the General Electric Co. as metallurgist and later became associated with Henry Disston & Sons, Tacony, Pa. In 1925 he was made metallurgist in charge of the metallurgical laboratory for this firm. Since 1926 Dr. Kinzel has been associated with various metallurgical units of Union Carbide & Carbon Corp. He was chief metallurgist of the laboratories from 1931 and in 1947 was made president. He is also vice-president of Electro Metallurgical Co., a division of UCC. Dr. Kinzel is chief consultant in metallurgy to the Los Alamos Laboratories and the Argonne National Laboratories of the AEC. During World War II he was consultant on metals to the Foreign Economic Administration, was project supervisor of the War Metallurgy Committee, and served on the Technical Industrial Intelligence Commission in England, France, and Germany as head of the Metals Section. He is a member of the Naval Research Advisory Committee, and the Metallurgical Advisory Board of the National Research Council. Dr. Kinzel presented the Howe Memorial Lecture at the 1952 Annual Meeting of the AIME.

N. K. Chen (p. 501) was born at Hunan, China. He attended Tangshan Engineering College in China and received his M.E. from Yale University in 1948 and D.Eng. in 1950. Now residing in Baltimore, Dr. Chen is research associate in the metallurgical section, dept. of mechanical engineering at Johns-Hopkins University. This Junior member enjoys music, playing chess, ping pong, swimming, and hiking in his spare time.

E. S. Machlin (p. 489) is now assistant professor at the dept. of metallurgy, school of mines, Columbia University, New York. Born in New York City, Dr. Machlin attended City College (B.M.E.); Case Institute of Technology (M.S.); and Massachusetts Institute of Technology (Sc.D.). From January 1942 to January 1948 he was an engineer with the National Advisory Committee for Aeronautics. He then was a research associate at Massachusetts Institute of Technology for two years and in October 1950 became an assistant professor. In July 1951 Dr. Machlin came to Columbia University as an assistant professor. A member of the New York Section, AIME, he is also a member of Sigma Xi and Tau Beta Pi. He had previously presented several papers before AIME. Among his various hobbies is listening to music in his spare time.

Morris Cohen (p. 489) was born in Chelsea, Mass. He attended Chelsea High School and graduated from Massachusetts Institute of Technology (S.B. and Sc.D.). Dr. Cohen was assistant professor physical metallurgy from 1937 to 1946 at M.I.T. and since then has been professor of physical metallurgy. Dr. Cohen is an AIME member and is now residing at Swampscott, Mass.

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● Most of you who use alloy steel have one problem in common today: you must continue to turn out products of the same quality your customer is accustomed to, while using steels containing a smaller percentage of many of the important alloying elements.

To do this, many of you must look to new methods of developing the ultimate in mechanical properties in the leaner alloy steels. One of the best ways to get those maximum properties from leaner alloy steels is to make use of the best available heat treating practices. Utmost care must be given to *all* phases of heat treatment: heating, *quenching*, and tempering—keeping in mind the "H" value of *your* water or oil quench tank, and the hardenability of the steel you are using.

United States Steel Company has developed an improved agitated quenching method to give you better results with leaner alloy steels—or with most all steels for that matter. We call it U·S·S Improved Heat Treatment. The actual process includes quench tank design plus the definite size, number, placement and powering of the propellers that agitate the bath. This quenching method extracts the heat evenly and rapidly from the entire surface of the part.

Close to a hundred manufacturers are already using this improved quenching method, and without exception report better heat treating results. They cite the following advantages over methods which provide for no agitation or inadequate agitation of the quenching medium:

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4. **Reduction or elimination of warpage and cracking through uniformity of heat extraction.**

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Teaching Personnel. (a) Economic geologist of metallic ore deposits, to teach ore deposits, polished surfaces and mineralogy. Knowledge and experience in metal mining desirable. (b) Extractive metallurgist, half time teaching, half time research. Research in field of ore preparation and concentration, including flotation. Should be able to teach these subjects and perhaps a course in process of production metallurgy. (c) Extractive metallurgist, to direct research project dealing with ore preparation and concentration, including flotation. Should be well trained and experienced in ore dressing and competent to direct men. Project will have six to nine men. Will be expected to take charge of project and obtain personnel. Rank and salaries dependent upon experience. Location, west. Y-660

Metallurgist, graduate, with five years or more experience in nonferrous metallurgical work. Knowledge of electrical equipment helpful. Will do research and administrative work on copper base and aluminum alloys used for electrical equipment. Salary, $7000 to $8000 a year. Company may pay or negotiate placement fee. Location, Alabama. Y-655

Engineers. (a) Tool designer, graduate engineer, with experience in designing tools, jigs, fixtures, and gages of high accuracy and close tolerance. Experience in draw die and punch design and fixtures for milling small parts preferred. (b) Production engineer, graduate, with five to ten years experience in either steel or brass, heat treatment of tools and dies of all types, control and measurement of grain size in brass. Location, Israel. Y-650

Lead Smelter Engineer. Familiar with the lead furnace operations and subsequent refining and alloying processes for a lead smelter operation based on the melting of battery lead scrap. Location, New York. Y-658

Assistant Foreman, graduate metallurgist for electrolytic copper refinery. Salary open. Location, Texas. Y-654

Senior Metallurgist for large research laboratory, with minimum of five years experience in base metal science including industrial research. Salary, £1200 a year plus cost of living allowance of about £100 a year, and variable metal bonus of about 60 per cent of basic salary. Free transportation, housing, etc. Location, Northern Rhodesia. Y-624

Concentrator Superintendent for large copper flotation concentrator, 35 to 40, with minimum of ten years' base metal flotation experience. Starting salary, £2000 a year plus cost of living allowance of about £100 a year, and a variable metal bonus of about 60 per cent of basic salary. Free transportation, housing, etc. Location, Northern Rhodesia. Y-625

Physical Metallurgists, research assistants and research associates, desiring opportunity to undertake graduate studies while working on Government aided research projects at leading eastern university. Salaries open. Y-631

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organize and direct research projects of fundamental nature in the flow and fracture of metals to work in SYLVANIA'S Metallurgical Research & Development Laboratories located at Bayside, L. I.

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BOX C-8 JOURNAL OF METALS

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BOX T-10 JOURNAL OF METALS

MEN AVAILABLE

Foremanship, supervision, also desire opportunity learn purchasing, brokerage, ores and metals or foundry work. Six years' process control and improvement, metallurgical accounting, production planning, supervise actual process and technical personnel in smelting and ore dressing. Age 40. B.S. in chemical engineering. M-581

Engineer, 28, family. Seeking Latin American opportunity. B.S. metallurgy. Graduate of American Institute for Foreign Trade. Knowledge Spanish. Aviator. Two years experience selling copper base alloys for mechanical and corrosion applications. Resourceful record. 1½ years factory experience with fabricating concerns. Presently located Chicago. M-636

Metallurgist, 23, B.S. metallurgical engineering. Presently employed in research. Desires change to obtain position offering diversified experience. Would prefer northeastern field, main interest applied research. Location is arbitrary. M-674

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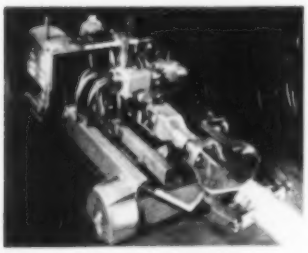
1—FORGING MANIPULATOR: An improved wedge action design in the work holding tongs mechanism of the *Sales-Bronius, Inc.*, auto-floor manipulator assures certainty of grip and maneuverability of hot stock during forging. These machines



come in sizes ranging from 1 to 10 tons carrying capacity. The rotating, tilting, vertical, and lateral motions of the work head guarantee complete control of the work during forging.

2—MERCURY VAPOR DETECTORS: Two redesigned portable mercury-vapor detectors for indicating concentrations of mercury that could be harmful to industrial workers, have been announced by *General Electric Co.* The electronic instrument is designed to give instantaneous indication of mercury vapor by resonant absorption of ultraviolet energy. Accuracy for determination is within ±5 pct.

3—HOLE PUNCHING UNITS: Type HS Hydra-Strip hole punching units for punching holes in mild steel up to ¼ in. thick are available from *Wales-Strippit Corp.* All component parts are built into the holders that keep the round or shaped punches and dies in perfect alignment for the life of the units.

4—DISK GRINDER: A high speed disk grinder, 9 in. long, weighing 4½ lb has been introduced by the *Balmes Corp.* Designed for one hand operation, it polishes, grinds, sharpens, and shapes all types of metals to a high degree of accuracy.

5—NICKEL COATING AL: A process for nickel coating aluminum has been announced by *United Aircraft Corp.* and the *Rust Laboratories Co., Inc.* A synthetic rubber compound is used to establish a bond between the aluminum and nickel plate. The bond material is sprayed onto aluminum to the required thickness. After drying the piece is plated with nickel by conventional means, the plate thickness depending upon requirements.

6—STAINLESS STEELS: New group has been introduced by *Allegheny Ludlum Steel Corp.* to help circumvent the critical nickel shortage. The new alloys use manganese to replace all or most of the nickel used in conventional chromium-nickel stainless steels.

7—BALANCING MACHINE: Advantage of this dynamic balancing machine is that it offers a simplified shop method of indicating unbalance in rotating parts weight up to 100 lb, without the necessity of making specially fitted bearings, adapters or universals. Manufactured by *Welch Mfg. Co.*, it is a floor model and speeds may be varied by changing the pulley size on the motor. The machine may also be ordered equipped with a variable speed motor.

8—MICROAMMETER: A new type micro-microammeter has been developed by *Beckman Instruments, Inc.*, that measures extremely small

currents with accuracy and convenience. Direct currents from 0.3 microamp to 0.3 micro-microamp full scale, with an absolute accuracy better than 5 pct in all ranges can be measured.

9—STEEL COATING: A new process called Leafcote has been announced by the *Mid-America Steel Warehouse, Inc.* The coating can be used as a prime coating or may be finished in any color desired. It is able to withstand high temperatures and is resistant to corrosion. After both sides of either a cold or hot rolled steel sheet have been degreased, pickled, and phosphatized they are heated, after which Leafcote is bonded and baked on for toughness and lasting adhesion.

10—PRECISION CASTING: Developed especially for high speed production of precision castings, this mechanically operated *Ajax-Northrup* induction furnace transfers molten metal from furnace to mold in any preset cycle. The furnace is

powered by a standard Ajax-Northrup 20 kw mercury hydrogen type converter, and operated at a frequency of about 30,000 cycles.

11—CHROME PLATING UNIT: A 250-amp unit has been added to the *Ward Leonard Electric Co.* line of industrial chrome plating equipment. The tool is designed for industrial chrome plating small tools or parts in large quantities or parts with areas to 125 sq in. Average plating time is 3½ min for cutting tools.

12—POWDER METAL PRESSES: Powdered iron cores on which coils, inductors, transformers, and similar products are wound, can be formed and molded into shapes and sizes and held to close physical and electrical tolerances. The *F. J. Stokes* R-4 eccentric cam single punch press applies pressure from above and below simultaneously, essential for parts requiring high and uniform density.

13—POTASSIUM CYANIDE: *Octagon Process, Inc.*, claims that bugs in bright plating and precision metal plating are eliminated and smooth operations assured, since no sulfide impurities are present.

14—CUTTING CARBIDE: A new grade of cutting carbide has been developed by *Newcomer Products, Inc.* It can be used at high machining speeds, but its greatest tool life is obtained at speed slower than those at which other grades of carbide can be successfully used.

15—GRINDER: A small hole grinder that may be equipped for external work is now offered by *Rivett Lathe & Grinder, Inc.* It grinds holes from the smallest up to 3 in. diam, with a 4 in. max depth, depending upon the diameter. It grinds externally up to 3 in. diam with a length of 4 in. The workhead, swiveling 90° each side of center for bevel and taper grinding, has the spindle mounted on super precision ball bearings, and has speeds of 200, 400, and 600 rpm.

16—SLIDE RULE: A new slide rule converts stainless steel sheet dimensions and gages into pounds and numbers of sheets. Setting the upper scale at sheet size in inches with lower scale set to indicate gage to be computed gives the number of sheets in a given weight or the total weight of a given number of sheets. *Atlantic Polishing Mill.*

17—ALUMINUM PASTE: Polychrome or metallic finishes are possible through the use of a new aluminum paste made by *Aluminum Co. of America.* It gives a brighter finish than has been possible thus far with other aluminum pigments. The metal content of the paste is 65 pct, sp gr is 1.47, wt per solid gal is 12.245, and it has a bulking value of 0.0820 gal per lb.

Free Literature

20—PROJECTION BALANCES: Selecta balances are equipped with a symmetrical double arm beam and are guaranteed for uniform sensitivity regardless of load. Pamphlet available from Sartorius Div., *C. A. Brinkmann & Co.* illustrates model and lists specifications.

21—SIGNAL BATTERIES: Publication of catalog section describing and illustrating Eveready air cell signal batteries has been announced by *National Carbon Co.* Construction and application data are described and operating characteristics are tabulated.

22—KIRKSITE DIES: A leaflet featuring a reprint of an article showing how Kirksite dies and other zinc die castings can be welded without melting the parent metal, is available from *Eutectic Welding Alloys Corp.* Case histories, photographs, data, and technical information on the reclamation and repair of a large Kirksite die as well as a delicate white metal scale balance arm are contained.

23—LEAD CLAD METALS: Booklet published by *Knapp Mills, Inc.*,

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Electro
SPECIFIC PURPOSE GRINDING WHEELS

contains information on history and development of Ferrolanc lead clad steel and Cupralum (cad clad copper).

24—PUMP CASTINGS: *Mechanite Metal Corp.* has recently published a bulletin on Mechanite pump castings. Photographs of pump castings and various types of pumps that utilize these castings are shown. Tables and charts are also included on the property evaluations made from recent tests covering wear, resistance to acid corrosion, impact, etc.

25—ELECTROPOLISHER: Bulletin is offered, providing information on the theory and practice of electrolytic polishing of metallurgical samples together with description of No. 1700 AB electro polisher. *Buehler Ltd.*

26—COMBUSTION INDICATOR: Photoelectric relay application, in the form of a Hazegage combustion indicator, is described in bulletin available from *Esi Instrument Co.* Wiring diagrams of installation and relay circuits are included.

27—NYLON LINED BEARINGS: Operating principles, design, and application of nylined bearings for rotation and reciprocation are described in brochure issued by *Thomson Industries, Inc.*

28—PLATING: Booklet *A Guide to Better Plating Power*, has been published by *Hart-Messing Corp.* Catalog contains descriptions, drawings, and photographs of the complete line of Sel-Rex selenium rectifiers. De power requirements are discussed with equipment recommendations to give efficient operation.

29—PLANT FACILITIES: Expanded plant facilities of *Allegheny Ludlum Steel Corp.* are described in bulletin just released. Data on equipment and production of the firm's Los Angeles forge plant and other plants are included.

30—PLATING EQUIPMENT: Bulletin on Sisalin sections has been issued by *Hanson-Van Winkle-Munning Co.* These sections, available with special stiffening impregnation for added cutting properties, can be combined to form wheels of any desired thickness for the plating industry.

31—TESTING MACHINES: Eight-page folder illustrates current Amsler machines for tests in tension, compression, torsion, shear, fatigue, bending and ductility. *A. J. Buehler Ltd.*

32—RUSTSHIELD: A chemical treatment that produces an oil-retaining rustproof surface for moving metal parts is described in booklet published by *Octagon Process, Inc.* Application methods and advantages of using Rustshield 2 on sliding and bearing surfaces are discussed.

33—MOTOR CONTROL CENTER: A new motor control center for use wherever two or more ac motors up to 200 hp, 600 v are controlled from a central location has been announced by *General Electric Co.* Brochure shows how to plan, install, and service the unit.

34—FLOW METERS: Literature giving full specifications, capacities, sizes, and dimensions is available from *Fischer & Porter Co.* Predictable metering floats for area flow rate meters make it possible to stock meters for immediate shipment.

35—COPPER ALLOY RODS: New publication B-14 on copper and copper alloy rods for screw machine use is available from *American Brass Co.* The booklet includes physical constants and properties on 46 free cutting and general purpose rods.

36—DUST COLLECTORS: Sizes and models of dustube collectors, cloth tube type, are illustrated in catalog issued by *American Wheelabrator & Equipment Corp.* Standard assembled and knocked down models have a range of air flow capacities upward from 252 cfm and filter air through various kinds of cloth. Specifications, construction drawings, and cutaway views are included.

37—X RAY DIFFRACTION: Goniometers, fluorescence analysis, electronic circuit panels, and table model spectrometers are just a few of the items discussed in this booklet released by *North American Philips Co., Inc.* Data is also included on special holders, crystal analysis equipment, thickness plating gages, and Geiger counters.

38—TANTALUM EQUIPMENT: Useful information on the chemical and physical properties of tantalum, is contained in booklet offered by *Fansteel Metallurgical Corp.* Detailed engineering descriptions of single and multiple tube bayonet heaters, heat exchangers, and instrument protection are included.

39—CARBON PRODUCTS: A new catalog section describing and illustrating *National Carbon Co.* carbon and graphite products is now available. Products in grades from porous to impervious for applications in the chemical and process, metallurgical, mechanical and electrical fields are fully described.

40—MACHINING ALLOY STEELS: Detailed drawings and tables that will assist the user of nickel alloy steels in determining the most economical and satisfactory combination of microstructure, tool form, etc. are given in bulletin available from *International Nickel Co., Inc.*

41—MICROSCOPE THEORY: A non-mathematical exposition of how a microscope works with some notes on conditions which influence optical performance is available in limited quantities from *Bausch & Lomb Optical Co.* Objectives, eyepieces, condensers, filters, and types of illumination are treated in a non-technical manner.

42—INDUCTION HEATING: Booklet obtainable from *Westinghouse Electric Corp.* presents case histories of how induction heating has increased production 50 to 2000 pct, reduced space up to 90 pct, and cut production costs. Modern induction heating apparatus are described as machine tools for hardening, heating, annealing, or joining metals in mass or batch quantities.

43—JET PIERCING: Detailed information on the fundamentals and practice of the Jet-Piercing process has now been made available in a pamphlet available from *Linde Air Products Co.* Actual piercing results are given, and new developments toward increasing overall process efficiency are presented and discussed.

Journal of Metals
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May

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ELECTROMET *Data Sheet*

A Digest of the Production, Properties, and Uses of Steels and Other Metals

Published by Electro Metallurgical Company, a Division of Union Carbide and Carbon Corporation, 30 East 42nd Street, New York 17, N. Y. • In Canada: Electro Metallurgical Company of Canada, Limited, Welland, Ontario.

Why 3 Per Cent Chrome Steel Makes Good Castings for Wear Resistance

Castings of 3 per cent chromium steel have been used in substantial tonnages for many years, for various equipment parts demanding good wear resistance. Such castings offer an excellent combination of hardness and toughness. Typical applications are crusher parts used in rock and ore-crushing equipment, swing hammers for pulverizing coal, railroad switch frogs, gears, pulleys, sheaves, and other castings that must meet severe conditions of wear.

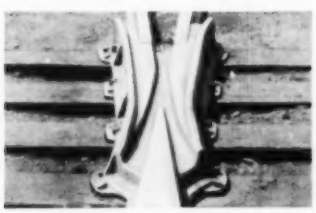

Fig. 1. Railroad switch frogs, which are subject to severe wear, give outstanding service when cast of 3 per cent chromium steel.

The 3 per cent chromium steels are normally produced in a carbon range of 0.30 to 0.50 per cent. They exhibit excellent depth-hardening properties, which simplify heat-treatment and insure uniformity throughout heavy sections. The analysis is usually modified by a molybdenum addition, since this element aids in increasing hardenability.

Fig. 2. Grating for top of shake-out machine is cast of 3 per cent chromium steel to give good wear resistance and long life.

Properties Improved by Heat-Treatment

The best properties of 3 per cent chromium steels are developed through heat-treatment. Generally, this consists of a normalizing treatment from 1650 deg. F., followed by tempering in a range between 1200 and 1250 deg. F., depending on the physical properties desired. Double normalizing is sometimes used to obtain further improvement in the grain structure. With carbon on the high side of the specification, air-quenched castings show a Brinell hardness number of over 450 in 3-inch sections. This hardness is practically uniform throughout the section. Oil quenching is employed to produce higher hardness and depth of penetration, and even in a 4-inch section, a hardness number of over 500 Brinell is obtained.

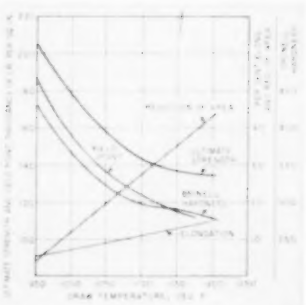

Fig. 3. These curves show the response to tempering of a 0.37 per cent carbon, 2.93 per cent chromium, 0.35 per cent molybdenum steel previously normalized from 1650 deg. F.

The steel also shows good response to tempering. After a normalize and a 1150 deg. F. treatment, it has a tensile strength close to 150,000 pounds per square inch, with an elongation value of about 12 per cent, and a Brinell hardness of about 300. When greater ductility is required, tempering should be done at higher temperatures. However, in such instances, some strength and hardness are sacrificed.

Fig. 4. Photomicrograph of 3 per cent chromium steel normalized from 1650 deg. F. and tempered at 1100 deg. F. (X250). The pseudo-austenitic structure is well suited to resist abrasion.

Effect of Other Alloy Additions

Molybdenum in the range from 0.40 to 0.55 per cent will improve depth-hardening characteristics and aid in reducing susceptibility to temper brittleness in the lower temperature ranges. If the molybdenum-bearing steel contains relatively high carbon (0.40 to 0.60 per cent) additions of approximately 0.08 to 0.10 per cent vanadium provide greater uniformity in hardening. Small additions of silicon increase strength and hardness and this element is sometimes increased to 0.80 or 1.00 per cent. Manganese is added in amounts between 0.50 and 0.80 per cent.

Metallurgical Service Available

When you have occasion to produce castings for applications involving severe abrasion and wear, it will pay you to investigate the advantages of using 3 per cent chromium steel. If you need help on some specific metallurgical problem, be sure to consult one of ELECTROMET's specially trained metallurgists and engineers. For further information, write to the nearest ELECTROMET offices in Birmingham, Chicago, Cleveland, Detroit, Los Angeles, New York, Pittsburgh, or San Francisco. In Canada: Welland, Ontario.

The terms "Electromet" is a registered trademark of Union Carbide and Carbon Corporation.

Books for Engineers

Treatise on Powder Metallurgy, Vol. III, by Claus G. Goetzel. *Interscience Publishers*. $22.00, 899 pp.—This third volume completes the most comprehensive and up to date series on powder metallurgy ever written. The first two volumes completely covered the historical, technical, practical, and mechanical aspects of the field, and are supplemented with this reference work. The first part of the book contains a classified and annotated literature section, and the second part contains a classified and annotated patent bibliography. Patents mentioned in Vols. I and II are located by item number in a cross index. Literature and patents up to 1950 are included.

The Science of Flames and Furnaces, by M. W. Thring. *John Wiley & Sons, Inc.* $6.50, 416 pp.—The author approaches the subject of industrial furnaces from the point of view that the furnace of the future will be a precision tool of the highest accuracy, controlled by instruments of the highest sensitivity. The book lays stress on the gap between the fundamental sciences and furnace design and use. Each chapter is summarized and a table of conversion factors and an index are included at the back of the volume. Diagrams and charts are used to illustrate the author's arguments.

The Welding of Non Ferrous Metals, by E. G. West. *John Wiley & Sons, Inc.* $8.50, 353 pp.—The book is written with two main classes of reader in mind. One group is the welding engineer, welding operator, welding instructor and trainee, and the other is the designer, works engineer, and metallurgist. Among the areas covered are properties important to welding, the fusion welding processes, resistance welding processes, pressure welding, the welding of aluminum and its alloys, and the welding of precious metals.

Utilization of Manganese, Nickel, Cobalt, Tungsten, Molybdenum. First report of the Joint Subcommittee, International Materials Conference. The report can be obtained by writing to Frank Standley, Office of Press and Public Relations, Room 222, 1625 Eye St. N. W., Washington, D. C. 94 pp.—The report represents the consensus of opinion of the Joint Subcommittee on Utilization and is the result of meetings held between June 11 and July 18. The subcommittee indicates lines along which savings in the five elements might be accomplished. A further series of meetings following the gathering of additional information has been suggested.

Cottrell, Samaritan of Science, by Frank Cameron. *Doubleday & Co.* $4.50, 414 pp.—The life of Frederick Gardner Cottrell, considered by many to be one of the leading scientific lights of the current century, is traced from boyhood through the various stages of his productive life. The book tells of the many patents which he turned over to a nonprofit foundation, and of the thousands of ideas he gave away. The book is based to a great extent on Cottrell's diaries and correspondence, and tries to show him as a man of great warmth, human foibles, and strong personality.

Electrolytic Manganese and its Alloys, by Reginald S. Dean. *The Ronald Press Co.* $12.00, 257 pp.—The book traces the growth of electrolytic manganese production since 1936 through the impetus it received from World War II explorations of U. S. sources. The scope of the book, however, has been restricted to the production of electrolytic manganese, to the properties and uses of the alloys in which it is necessary, and to alloys in which electrolytic manganese produces properties significantly different from the use of other manganese types. Much of the material in the book was obtained from reports issued by the Bureau of Mines.

Production Processes, Their Influence on Design (Machine Design Series Vol. II), by Roger W. Bolz. *Penton Publishing Co.* $7.50, 357 pp.—The book groups a wide range of manufacturing methods under four main headings: Casting methods—sand, permanent-mold, centrifugal, investment, and others; molding methods—powder, plastics, rubber, ceramics; fabricating methods—welding, brazing; and treatment methods—heat treating, shot peening. Each chapter includes design detailing, material selection, and shop tolerances.

The Manufacture of Iron and Steel Vol. II, by G. Reginald Bashforth. *Chapman & Hall, Ltd.* 45s, 461 pp.—A complete treatise on the subject of iron production is formed with the publication of the second volume in the set. The latest volume deals with the acid and basic bessemer processes, the acid and open hearth processes, electric furnaces, ingot production, side-blown converter practice, special steels, steel works instruments, and refractories.

An Introduction to the Engineering Profession, by John G. McGuire and Howard W. Barlow. *Addison-Wesley Press, Inc.* $5.00, 260 pp.—The engineering field is given a comprehensive survey from the point of the student interested in the nature of the work, aptitudes necessary, preparatory courses, and the future prospects. One section is given over to illustrative problems in various branches.

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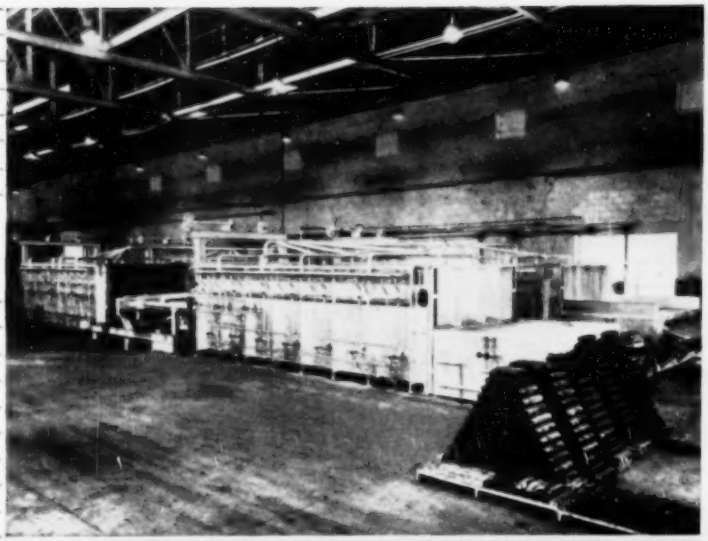

Loftus heat treat line for treating shell cases provides completely automatic operation from loading conveyor to unloading conveyor.

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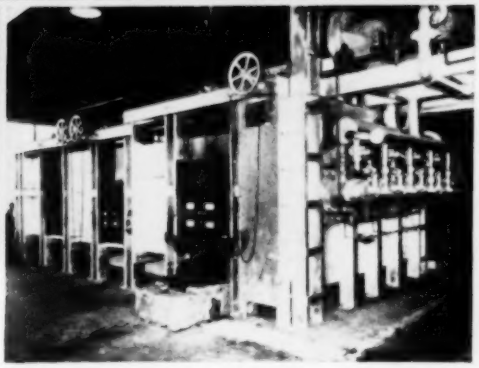
Production rate increases of 50% have been achieved through installation of this Loftus strand furnace.



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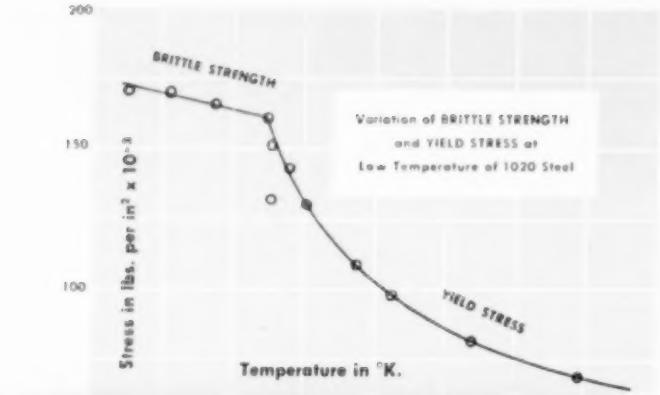

1020 Steel at 61.5°K.

A need for measurements of brittle strength as a function of temperature prompted the results shown in the curve above. Several samples of hot-rolled 1020 steel were tested at various temperatures in the interval 12°K. to 61.5°K. All exhibited brittle fracture with no reduction in area. At 75 K., however, a definite yield point was observed and the increase in length before rupture was unexpectedly large. Several additional specimens were broken at temperatures lying between 61.5° and 75 K. The results indicate a sharp transition near 61.5°K., below which no reduction of area occurs and above which the reduction of area increases rapidly as the temperature at which the sample is broken rises above 61.5°.

The ADL Collins Liquid Helium Cryostat, by providing test chamber temperatures from ambient to −271°C., makes many research projects like this possible. Superconductivity, resistance minima in metals at low temperature, and thermal conductivity are a few of the studies utilizing the ADL Collins Cryostat, the basic tool of a new research frontier.

For further information request Bulletin JM-2 including details of the Collins Helium Cryostat and a reprint of "Fracture and Yield Stress of 1020 Steel at Low Temperatures" by A. S. Eldin and S. C. Collins.

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Industrial Notes . .

• About 1000 designers and engineers will move to Willow Run when the Chase Aircraft Co. is transferred from West Trenton, N. J. The Kaiser-Frazer Corp. is making the change in preparation for production on a new Air Force transport. Personnel and equipment will be relocated in about three months. The new aircraft, C-123B will be produced on a line similar to the one used by Kaiser-Frazer to manufacture the Fairchild C-119. The Chase plane will be produced in greater numbers than is presently planned for the Fairchild.

• **Titanium Co. of America has been formed by the Christiansen Corp., Chicago producers of aluminum and magnesium alloy ingot. The new company has been chartered in Delaware and will produce wrought titanium products for industrial and military buyers. It is wholly owned by Christiansen. The plant will be located in East Chicago.**

• An addition to the Wales-Strippit Corp. North Tonawanda, N. Y. plant, will be built at a cost of approximately $70,000. The addition is the fourth since 1949 and will boost total space to 65,000 sq ft.

• *The United States will get Belgian Congo tin at $1.20¾ per lb. delivered at American ports, under a contract signed by the RFC and the Tin Producers' Committee of the Belgian Congo and Ruanda Urundi. The contract is for two years, but is renewable from year to year. If a more favorable price is granted other countries, the contract price increases automatically and in proportion. More than half of the produced tonnage of the Belgian Congo is covered by the pact.*

• A new brazing technique is making possible the use of better manufacturing methods in the electronic industries and better cutting tools for metal working shops. Scientists, in a report for the Commerce Dept., say the new technique has been carried out in controlled atmospheres and vacuum, with the use of fluxes. A series of experiments on metals and nonmetallic materials, with active metals such as titanium, zirconium, columbium and tantalum, have been carried out. Carbides, refractory oxides, stainless steel and chrome-iron type alloys have been brazed. The active metals used in the technique are reported to wet both metals and nonmetallic materials equally well. This report, *PB 100 109, Metal to Non-*

metallic Brazing, is available in microfilm at $2.00 and $3.75 in photostat, from the Library of Congress, Photoduplication Service, Publication Board Project.

• **The metals industry is watching the recent surge in development of rare earth elements, cerium, neodymium, lanthanum, gadolinium, and others. One survey states that more than 150 known minerals contain these elements, with important sources in Brazil, India, Malaya, Australia, Norway, and the United States. Present mining operations appear adequate to supply current demands.**

• Malone Metal Powders, Inc., Malone, N. Y. is the latest firm to enter the field of production of the special metal powders needed by various military and civilian industries. It will be operated in connection with the Malone Bronze Powder Works, although established as a separate corporation.

• *The National Production Authority has moved to ease bottlenecks in the flow of components and parts into military, atomic, and machine tool production. Prime defense contractors may pass down, to all their subcontractors, orders for components and noncontrolled materials carrying top defense, atomic, and machine tool priorities. The prime contractors will also be able to pass along top priority orders for steel, copper, and aluminum controlled materials by May 1.*

• General Electric is planning to convert its Scranton, Pa., home dishwasher plant to the production of electronic tubes. Conversion and installation of equipment is expected to start during April. The company is planning to spend several million dollars for the changeover.

• **The recently completed Bjorksten Research Laboratories' building at Madison, Wis. will house a program intended to supplement research already being carried out at the Laboratories' Chicago headquarters. Solution of ore beneficiation and materials processing problems is the current problem of the mining and metallurgical staff. Flotation of low grade iron ores and the use of radioactive tracer methods in the solution of mineral beneficiation problems are among the latest projects of the group.**

• *U. S. Steel Co. will build a steam and electric power plant at its Ohio works.*

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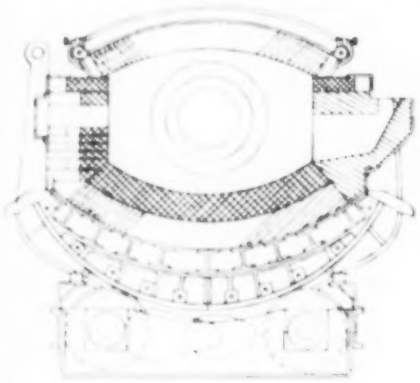
Here's how to HOLD THAT LINING in your holding furnace

Operators of Whiting* Cradle and similar types of holding furnaces use Taylor Sillimanite (TASIL) brick and cement to prolong the life of refractory linings. Recommended practice is to "*balance*" the super-duty fire brick lining with 9" of TASIL brick, laid in TASIL No. 301 Cement, for both side walls and bottom, in the areas subject to the damaging wash of molten iron and slag. (See refractory construction shown in engineering drawings below.)

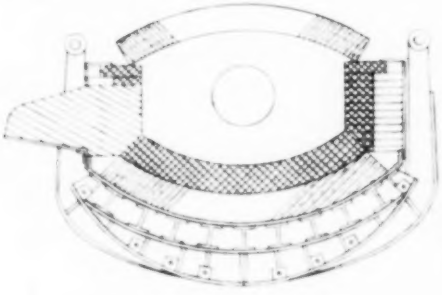
A TASIL "balanced" lining at one plant is averaging 6-8 weeks on side walls and 9-12 months on bottoms, with patching. TASIL was tried after a super-duty fire brick lining failed in three days because of joint attack and severe erosion at the metal line. This furnace is fired with pulverized coal and runs 700 tons per week of grey iron, tapped from cupola at 2750° to 2800° F.

Wherever you use fireclay-base, high alumina, kaolin or similar refractories, TASIL will give more effective service. Let a Taylor field engineer discuss with you the savings Taylor Sillimanite can make in your plant.

Tasil "Balanced" Lining In Whiting Cradle Furnace



Section through Pour-in Spout



Section through Pour-out Spout

TASIL sidewalls and bottom 9" thick. TASIL top course in sidewall 13½" thick.

▨ = Taylor Sillimanite

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THE DRIFT OF THINGS

by Edward H. Robie

NEVER before have the annual company reports in the mineral industry field exhibited the typographical art so abundantly as does the current crop. Time was when most company reports made a drab appearance and dry reading, mostly confined to financial data and text that gave little information to the public or technical men. Now, the dollar statistics assume less importance. Considerable information is given on what is going on at the company's plants, new equipment being installed, new methods, properties under development, ore reserves and grades, and similar information of interest to professional men working in the field. We have one suggestion for further improvement: The names of the officers and directors of the company are always given, but only a few companies give the names of the principal operating officials. We think, in the case of a mine for example, that the name of the general manager, his assistant, the mine and mill superintendents, and any other top operating officials who have been largely responsible for the success of operations, are worthy of mention. The reports are now widely read and this recognition is due them.

Conspicuous among the annual reports that we happen to have seen, in point of typographical attractiveness, are that of the Texas Co., celebrating its fiftieth anniversary with a gold-plated cover and gold printing inside; and that of Noranda Mines Ltd., with a red and black cover that would attract attention anywhere.

Comment on economics, taxes, and labor give an excellent picture of what our industry is facing. Consider the following, from the report of the Union Oil Co. of California:

> "Your Company, as well as industry generally, is finding it extremely difficult to maintain the financial resources necessary to cover the high cost of replacing raw material reserves and facilities and at the same time expand its operations. Not only are taxes severely limiting the accumulation of capital by industry, but they are reducing the savings of individuals, the basic source of risk capital, and eliminating the incentives for investment. Simultaneously, costs industry is prevented by price control from recovering most increases in cost brought about by inflationary wage increases and taxes.
>
> "As a result of the inflation induced by unbridled Government spending, we can no longer regard profit as simply the difference between sales revenues and recorded costs. The reason is that only a portion of recorded costs are expressed in today's dollars. Depletion and depreciation costs, which provide for the recovery of capital invested in properties and facilities are limited to the number of dollars initially invested. Because of the decline in the purchasing power of today's dollar, the amounts set aside for depletion and depreciation are simply not enough to meet replacement costs. Therefore, it is a literal fact that a substantial portion of the amount reported as profits is actually not profit, but should be recorded as a return of capital needed to keep the Company a going concern. It is not too much to say that this portion of apparent profits on which your Company is taxed, represents an involuntary liquidation of capital assets. There is a serious doubt whether your Company's reported profit figures, in common with most of industry, have any real meaning.
>
> "It is seldom recognized that the purchasing power of industry's dollar has declined even more than has that of the individual. During the past 10 years, the wholesale price index, a measure of industry's cost of doing business, has increased 127%, while the consumer's price index has increased 76%."

A Practice That Should Spread

An idea materialized at the recent Annual Meeting that we should like to see extended. Whether held in New York, San Francisco, Los Angeles, Chicago, or St. Louis, a comparatively small proportion of the Student Associates and Junior Members of the Institute are able to attend its Annual Meetings. They can gain a great deal in technical knowledge, in widening their acquaintance, and in absorbing the spirit of a professional society in action by coming to such a meeting, but must perforce be absent because of either the cost or the requirement of their employer or their school that they should remain on the job.

The problem was completely solved for 37 young men last February. A picked group of that number from the School of Mines and Metallurgy at Rolla, Mo., was excused from classes for a week and organized by J. D. Forrester, Chairman of the dept. of mining engineering. The Sinclair Coal Co., Kansas City, Mo., through the good offices of Thomas C. Cheasley, footed the bill of $1300 for a bus from Rolla to New York and back. Free registration at the meeting was provided by the Institute, and hotel expense was kept nominal by lodging most of the group at Sloan House, the neighboring YMCA, at $1.35 per person per day. We suspect that the AIME Directory ten years hence will show practically every one of these young men as a member.

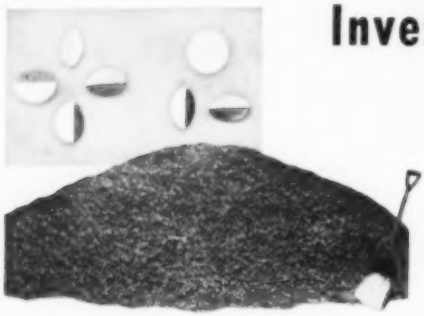
Many other companies would doubtless do something similar if the head of the department at a college would promote the idea. Let us have more such trips to the Los Angeles meeting next February.

Junior Members cannot be similarly grouped for attendance at an Annual Meeting, but their employers can offer such a trip, with a part, at least, of expenses paid, as a prize for conspicuously satisfactory work. From the company standpoint the money would be well invested on several counts. If you, who read this, happen to be the head of a company or local operation, why not announce, now, that one or more of your Junior Members will have the opportunity to go to the Los Angeles meeting? Alert Junior Members will doubtless find a way of bringing this suggestion to the attention of their boss!

A Complete Library

The statement has been made, and we believe never questioned, that the AIME Transactions constitute "the most extensive and authoritative library extant on engineering and technology in the mineral industry." Carl A. Zapffe evidently thinks so, for headquarters recently helped him complete, so far as possible, his library of the Transactions. He recently wrote, "Thanks again for the numerous favors connected with this operation. You can get one assurance from it, and that is that at least one AIME member will have paged through and studied every single volume of the Transactions since 1871! I expect to know everything that the Institute has done before these babies take their place on the shelves."

Dr. Zapffe is a metallurgist and according to the last Directory is available for consulting work. A word to the wise is sufficient!



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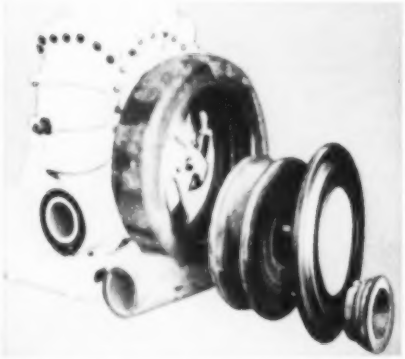

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New York 17, N. Y.

American
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Irvington 11, New Jersey

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Palmyra, New Jersey

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New Castle, Pa.

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CENTRAL SECTION...

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Marshall, Mich.

The Babcock & Wilcox Co.
85 Liberty St.
New York 6, N. Y.
(Plant: Barberton, Ohio)

Brake Shoe
& Castings Div.
American Brake Shoe Co.
104 N. Wabash Ave.
Chicago 4, Ill.
(Plant: Mellose Park, Ill.)

Frank Foundries Corp.
2020 3rd Ave.
Moline, Ill.

Griffin Wheel Co.
443 N. Sacramento Blvd.
Chicago 12, Ill.

Wells Manufacturing Co.
7800 N. Austin Avenue
Skokie, Ill.

Eagle Iron Works
129 Helmick St.
Des Moines, Ia.

Helmick Fdry. Mach. Co.
8th St. & Belt Line
Fairmont, W. Va.

Carondelet Foundry Co.
2101
S. Kingshighway Blvd.
St. Louis 10, Mo.

Keller Foundry Co.
1010 E. Jackson Ave.
Knoxville, Tenn.

Arkansas Foundry Co.
1503 East Sixth St.
Little Rock, Ark.

WESTERN SECTION...

Eagle Foundry Co.
73 Horton St.
Seattle 4, Wash.

Union Iron Works
Box 2135
Spokane 2, Wash.

Caird Engineering Works
Helena St. &
Montana Ave.
Helena, Montana

Pacific Ball Mfg. Co.
P. O. 106
Southgate, Calif.

Pacific Foundry Co., Ltd.
1500 19th St.
San Francisco, Calif.

Stanley Foundries
6009 Santa Fe Ave.
Huntington Park, Calif.

Capitol Foundry Co.
Phoenix, Arizona

Derbyshire Steel Co., Inc.
P. O. Box 152
El Paso, Tex.

Texaloy Foundry Co.
1407 Hoefgen
San Antonio 3, Tex.

THE INTERNATIONAL NICKEL COMPANY, INC.

67 WALL STREET
NEW YORK 5, N. Y.

Bohn Aluminum & Brass Corp. of Detroit, and the Glidden Co., Cleveland, have combined forces for a broad research program in the development of titanium. Both firms are interested in the production of the pure metal, its compounds and alloys and in the fabrication of ductile titanium and its alloys. Work will be conducted at the Glidden, Baltimore laboratory and at the Bohn laboratory in Detroit.

A Bureau of Mines report says laboratory tests on titanium ore samples from the Christy deposit in the Magnet Cove area, Hot Springs County, Ark., have produced concentrates containing 91 pct to more than 92 pct titanium oxide with fair recoveries. Results of the mineral dressing research show from 55 pct to 60 pct of the titania in the samples may be concentrated by flotation into a product containing the reported concentrate.

The new integrated steel works constructed by the state controlled Finsider organization at Cornigliano, Italy will begin partial operation with the blowing-in of one 750-ton blast furnace during April. A similar unit will be activated in August, when five open hearth furnaces of 180-ton daily capacity each, also start production. The American equipped plant will have two 28-coke oven batteries with a daily peak of 1400 tons. The foundations for a hot strip mill to produce 700,000 tons annually have been laid. Main product of the plant will be steel sheet.

Electro Metallurgical Co., a division of Union Carbide & Carbon Corp., plans to improve its Marietta, Ohio, plant to the point of producing about 6000 tons of electrolytic manganese annually. The company is operating its sixth large electrolytic furnace at Marietta, and has eight more furnaces under construction in order to meet the demand for ferroalloys.

United States production of electrolytic manganese received additional impetus through an agreement reached between DMPA and the Electro Manganese Corp., Knoxville, Tenn. The $2.25 million loan will be used to enlarge facilities, and enable a doubling of the 7.2 million lb now produced annually.

United States, Canadian, and South African laboratories combined to establish a reference standard sample for metallurgical chrome through cooperative study. Careful analysis of the ore, containing 50.96 pct Cr_2O_3, for chrome oxide, iron, silica, alumina, and magnesia, fills an industrial need for a reference standard having a chrome oxide content higher than the chrome refractory containing 36.97 pct Cr_2O_3 now obtainable from the National Bureau of Standards. Portions of the sample and copies of the analysis certificate can be had from Merton H. Davey, Andrew S. McCreath & Son, Harrisburg, Pa.

Sierra Leone powdered iron ore concentrates will probably be available in increasing amounts in the next few years. The present rate is about half a million tons annually, with a goal of one million tons in view. Trials are progressing with the pelletizing of the ore at a pilot plant of the Redcar works of Dorman, Long & Co., Ltd. Present production is about half ton an hr.

The International Materials Conference reports free world production of tungsten in the second quarter of 1952 will be 20 pct above the first quarter. Molybdenum output will rise about 10 pct for the same period. Production outside of the Iron Curtain in the first half of 1952 will be approximately 8200 metric tons metal content of tungsten. About 10,016 metric tons of molybdenum will be produced, it is estimated.

Anodes are cast at the rate of 40 tons per hr on each of the two 40 ft hydraulic driven casting wheels shown. Two 200 ton anode refining furnaces supply each wheel.

Production at Garfield

World's Largest Copper Smelter

by R. Thompson

GARFIELD Smelter of the American Smelting & Refining Co. is the largest primary copper smelter in the world. During critical stages of short supply of copper early in World War II, it exceeded its previous normal production capacity by about 50 pct with no substantial expansion of existing facilities. The smelter is located 20 miles west of Salt Lake City, near the southern shores of Great Salt Lake. Current daily production is 775 tons of copper in anode shapes and 430 tons of sulphuric acid (Basis: 100 pct acid.) Precious metals and some impurities are carried through smelting units with the copper phase and are separated at electrolytic refineries. Lead is recovered as a leady dust from shelter fumes in flues and Cottrell electrostatic precipitators. As a custom smelter, Garfield receives supplies of the Utah and other intermountain areas. The principal source of concentrates, however, is the mining and milling operation of Kennecott Copper's Utah Div. Kennecott's Bingham ore, a porphyry copper averages less than 1 pct copper and concentrates received from the mills at Arthur and Magna are about 31 pct.

The present level of operation requires a total force of nearly 1400 employees. Approximately 60 pct of the personnel live in the greater Salt Lake City area, and the balance live in nearby Magna and Garfield. Bargaining units for operating personnel and clerical employees are locals of the United Steel Workers of America, CIO.

In keeping with company practice, an active safety organization, headed by a full time safety engineer, is maintained. The organization investigates and provides appropriate safety and protective equipment, publishes and distributes a monthly safety news letter to all employees, and distributes industrial safety information to plant supervisors. Safety glasses with necessary optical corrections are provided and employees may purchase safety shoes at cost. Recently, 20 pct of the plant's daily labor force was given a 20 hr standard Red Cross course in first aid. As part of the organization, representatives from each plant department meet monthly with the safety engineer for discussion of plant safety practices and showing of safety films.

Every effort is made to improve smelter working conditions. Although obnoxious fumes, dust, and heat are inherent to its operations, elaborate dust control and ventilating equipment are installed whenever practicable. The sample mills and bucking rooms are extremely well hooded and air conditioned. Matte and slag launders are hooded and the irritating sulphur dioxide gas and fumes are vented to atmosphere outside working areas. Whereves temperatures are excessive, fresh air is filtered, washed and blown to the working area. All converter crane cabs are completely enclosed and air conditioned.

Operations at Garfield have paralleled many of the advancements made in the copper smelting industry since the turn of the century. In 1905, ground was broken at the present site for the construction of the smelter by an affiliated company of the American Smelting & Refining Co. This was for the smelting of gravity concentrates that would be made available by the large scale development of the Bingham ore body by the Utah Copper Co., now a division of Kennecott Copper Corp.

First smelting at the new plant began in September 1906, and, at the end of the year, 5500 tons of copper had been produced in smelting 33,000 tons of concentrates, crude ores, and fluxes. Garfield has produced some 6 million tons of copper by smelting over 40 million tons of solid materials. A large and ever growing monument to the smelter's past production is its dump which contains well over 25 million tons of once molten slag.

Originally the smelter was to consist of eight roasters, two reverberatory furnaces, two blast furnaces and six converter stalls. In keeping with practice of that early date, the reverberatories were 19 ft wide and 119 ft long, center charged, and fired by hand shovelling coal onto grates. Waste heat

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This paper will be presented at the Pacific Northwest Joint Conference, AIME, Spokane, Wash., May 8 to 10, 1952.

boilers on these furnaces were arranged in tandem. Smelting capacity was small and generally limited to about 150 tons per furnace day. The converters were 96x138 in., acid lined shells which, after finishing from two to four 10-ton charges, required new linings of rammed silica. By 1909, the operation had expanded to 38 roasters, 5 reverberatories, 4 blast furnaces, and 9 converter stalls.

Following this period of expansion, major changes in operation and equipment were made. Oil firing of the reverberatories was adopted in 1911, only to be replaced by pulverized coal in 1915, and finally by natural gas in 1932. Charging methods were revamped and ultimately both center charging and side charging replaced by the practice of gun feeding. Developed at Garfield by R. A. Wagstaff in the late 1920's, gun feeding was a logical consequence of smelting flotation concentrates.

The impact of flotation was felt in another department. As a result of the availability of large tonnages of fine concentrates not suitable for blast furnace smelting together with decreases in receipts of high grade crude ores, blast furnace operation became uneconomic. With increases in reverberatory smelting capacities, crude ores could be smelted at lower costs in the reverberatories even with added costs for further size reduction. Garfield's last blast furnace campaign was completed in 1922 after treating over 5 million tons.

Converter slag, which originally had been cast or granulated and returned in the solid charge to reverberatories and blast furnaces, was returned molten to reverberatories. Thus, the burden of reverts was reduced, percentages of concentrates and ores in the furnace charge were increased, and the fuel efficiency of the overall operation was improved.

In 1909, Garfield operated its first basic lined converter. The introduction of this unit was an important change and the subsequent development of basic converting was a major contribution to today's large tonnages. The first basic converters, which soon replaced all acid lined units, were 10x26-ft shells. In 1916, No. 8 converter, a 13x30-ft basic lined unit, was placed in service. Replacement of the small converters by units similar to No. 8 was completed by 1940. Whereas in early practice, the acid lining supplied silica, basic converting required the external addition of siliceous fluxes, and for some time fluxes were charged through the converter mouths by overhead cranes. By 1915, the Garr gun had been developed at Garfield. This device permitted flux additions to be made through the ends of converters during the blow without danger from blowouts when using wet fluxes.

In 1916, a lead chamber plant with pyrite roasting facilities was erected to supply sulphuric acid for use in flotation mills of the Utah Copper Co. Its daily output was 40 tons of 77 pct acid. When acid flotation circuits were discontinued in the early 1920's, its production was sold on the local market. Demand for this weak acid was limited and the old chamber plant was abandoned in 1937, when a modern contact plant was constructed. This plant uses a vanadium oxide catalyst and produces acids of varying strengths, including oleum.

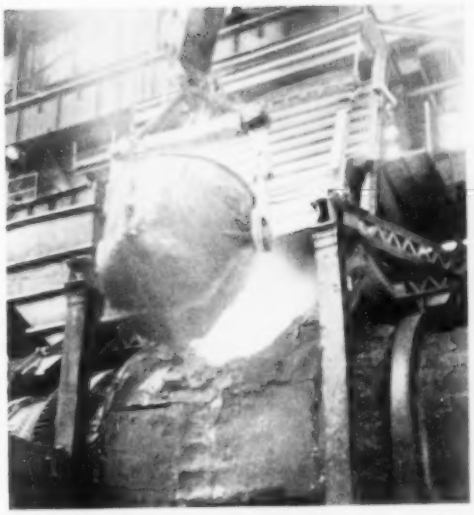
Current operations at Garfield are similar to those of many custom copper smelters. Ores and concentrates are received in the plant yard via one of three railroads, Kennecott's haulage line, the Denver & Rio Grande, or the Union Pacific, and via trucks. All incoming materials are sampled for moisture, weighed, and then spotted at appropriate unloading points for subsequent metal-content sampling and distribution.

Unloading and sampling of Kennecott concentrates are accomplished in one operation by Martin machines, a Garfield development, and the concentrates are conveyed by belts to bins for bedding. Crude ores are unloaded into separate bins, crushed, sampled, and distributed to either roaster ore bedding bins, converter flux bedding bins, or stock piles.

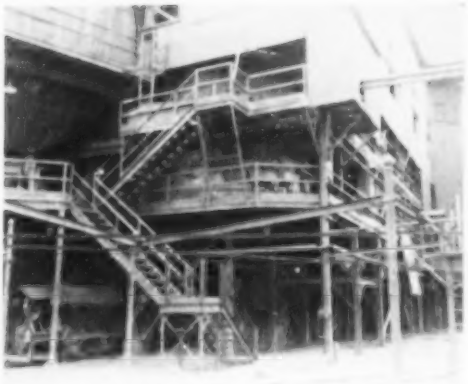
Smelter requirements for lime are satisfied by using an oolitic beachsand found in beds between the smelter and the Great Salt Lake. This material is a cheap source of lime, easily reclaimed with no expensive quarrying or crushing. Since 1908, over 2½ million tons have been utilized. During periods of low copper intake, this inexpensive material has permitted profitable smelting of siliceous gold and silver bearing ores with resultant slags containing as high as 43 pct silica and 22 pct lime.

The bedded roaster charge, consisting of ores, concentrates and limesand, is hauled from bins to roaster feed hoppers in larry cars by small electric locomotives. Currently operating are eight Call and Wagstaff roasters with eight hearths, and four to six McDougalls with six hearths. All of these roasters are 19½ ft diam, have a capacity in excess of 200 tons per day, and are fired with natural gas.

Calcines, the roaster product, are hauled to reverberatory smelting furnaces in 6-ton larry cars. Five reverberatories are available; however, only three are required for present operation. Products of the reverberatory furnace are matte, a molten solution of copper and iron sulfides, and a dump slag consisting of iron and lime silicates. In the furnaces, slag and matte separate by gravity. Slag is skimmed through a water-jacketted hole at the frontwall and hauled to the dump in pots drawn by electric locomotives. Matte is tapped through holes along the sidewalls of the smelting zone and runs by gravity into ladles set in the converter aisle.



Matte from the reverberatory smelting furnaces, transported in ladles by a 60 ton overhead bridge crane, is poured into a converter



A multiple hearth roaster (center) produces calcines, which are hauled by lorry trains (lower left) to reverberatory smelting furnaces.

Ladles of matte are transferred by overhead cranes and the matte is charged to converters.

An impressive sight is the 800 ft converter aisle. With as many as eight converters blowing, some skimming, some taking matte, and with the transfer and handling of molten materials by four overhead cranes, the view is spectacular. In addition to the converters, two blister copper holding furnaces are located near the center of this aisle.

Converter fluxes are hauled in larry cars from bedding bins to hoppers at each converter. Fourteen pound air for converter blast is supplied by the smelter powerhouse. Liquid slag, which contains considerable quantities of copper, is returned to reverberatories, and blister copper is transferred to the holding furnaces, from which it is taken to anode dept. furnaces as needed.

The anode dept. was completed in the summer of 1950. Previously, all copper was cast into 470-lb blister bars. Presently, cast anodes are shipped to Kennecott's new refinery at Garfield and to company plants at Baltimore and Perth Amboy. Four anode refining furnaces are served by two 40-ft hydraulic driven casting wheels. The 14x27-ft furnaces are oil fired, tilting type, and have a capacity of 200 tons each. Two furnaces are set tangential to each casting wheel. Poling is done through a door in the center, charging and firing through opposite ends. Although a portion of the blister casting equipment remains as a standby unit, the entire production is cast into anode shapes.

The interior of a gas fired, brick lined reverberatory furnace is shown while being rebuilt.

The first Cottrell electrostatic precipitator to be used in any smelter was erected at Garfield in 1915. Currently, all smelter gases are treated by this method. Dust recovered in the roaster-reverberatory system is high in copper and is returned to the reverberatory furnaces. Leady dust from the converter system is shipped to a lead smelter for retreatment.

Until 1945, all converter gases passed through pipe and plate treaters in series before being discharged to the atmosphere. At that time, Garfield began utilizing these gases for sulphuric acid production, however, only 10 to 15 pct of the total converter gas volume was used in this undertaking. Recently, all converter gases have been diverted to a new Cottrell from which any portion of these gases is available for sulphuric acid production. The unused portion is exhausted into the roaster-reverberatory system beyond its Cottrell, and the old converter system and stack are to be abandoned. After initial Cottrelling, gases for acid production are scrubbed, passed through a wet Cottrell, and delivered to the contact plants. Acids of varying strengths are shipped on purchaser's specification. Expansion in the intermountain states, particularly in the steel, fertilizer, oil and sugar industries, has resulted in tremendous increases in demand for sulphuric acid. Three contact plants are now in service and the erection of a fourth plant is contemplated.

Making sulphuric acid from converter gases introduced new problems. A contact acid plant utilizes heat generated by the exothermic conversion of sulphur dioxide to sulphur trioxide to preheat incoming gases. When using gas from roasters, its relatively uniform SO_2 content and volume gave little variation in the overall heat balance. In contrast, converter gases vary widely in composition, and external heat must be applied during periods of lean gases. Every effort is made to maintain maximum sulphur dioxide concentration. Relatively tight fitting hoods at converters and automatic dampers in the flue system are installed to reduce dilution with air, and converters are scheduled to minimize the effects of necessary but intermittent servicing.

Metallurgical control of smelting can be accomplished best by proper bedding. Garfield's practice is to bed concentrates, ores and fluxes so as to produce a matte grade of about 43 pct copper and slags of 38 to 40 pct silica. This is accomplished through elimination of about 20 pct of the sulphur by roasting. Past experience indicated that this slag analysis is optimum for Wagstaff gun-feeding of reverberatories. With this feeding, best smelting is obtained when the charge floats on top of the bath and spreads the length of the furnace. This spreading permits the charge to absorb maximum heat in a minimum time. Obviously, if the slag has low viscosity, resulting from low silica content, it will be thin and allow the charge to sink before smelting is completed. If the slag is too refractory, high in silica, it will be viscous and the charge will not spread. Under either condition, the smelting rate decreases markedly.

The three larger reverberatory furnaces are approximately 25 ft wide and 120 ft long, inside. Fur-

nace crucibles are constructed of chemically bonded magnesite brick to a height about 10 in. above the normal matte line. The sidewalls and sprung arch roofs are built of a local silica brick. Water jackets are installed above and below the gas burners at the bridgewall, around the converter slag return launder, and at the skimbay and frontwall. No jacketting is done along the sidewalls, but cooling air is sprayed on the outside of the sidewalls at the slag line. Occasionally, it is necessary to make hot patches and replace a portion of the silica brick in the sidewalls. Primary arches are ribbed in the smelting zone. When brick gets thin, a secondary arch is placed between these ribs. Silica slurry is applied while the furnace is in operation. The usual life of the reverberatory has been prolonged by the application of this slurry and is no longer a major problem. Campaigns now extend over an 18-month period.

Garfield has developed its own burners for gas firing the reverberatories. When natural gas was introduced, several types of commercial burners were tried with only moderate success. After several years of experimenting, a multiple jet burner was developed. The burner consists of 38 jets or nozzles centered on Venturi tube openings. Carefully sized holes are drilled in the nozzles and the Venturi tubes are machined in cast iron blocks faced with a replaceable heat resistant casting. Approximately 75 pct of the air required for combustion is inspirated through the throats of the Venturi tubes. The larger furnaces have eight such burners. With this arrangement, good mixing is accomplished and the flame is controlled easily. Maximum smelting usually results when burning about 3½ million cu ft per day, for a gross ratio of about 3¼ million Btu per ton of solid charge smelted. Solid charge averages over 900 tons per furnace day.

Present converter practice results in exceptionally long campaigns. A lining of hard-burned magnesite brick will produce in excess of 50,000 tons of blister copper over an 18 month period. Converting is a two-stage, batch process. In the first stage, or so-called slag blow, a portion of the sulphur in the matte is eliminated. At the same time the iron oxidizes, combines with siliceous fluxes, and is removed as slag. During the slag blow, matte and fluxes are added and slag removed at intermittent periods until the equivalent of 60 tons of copper is contained. After the last skim of the slag blow, converting advances to the second stage or finish blow. The remaining bath consists of white metal, a copper sulphide. With continued blowing, the sulphur oxidizes and blister copper results.

Because of the presence of small amounts of undesirable lead in the blister copper, it is practice at Garfield to have a third blowing period, known as the overblow. After formation of blister copper, lead-free siliceous flux is added and blowing resumed until the flux has combined with copper oxide to form a fluid slag. This overblow period lasts about 20 min.

Metal oxides, and particularly copper oxide, are highly corrosive to magnesite brick. To maintain converter linings, especially at the tuyere line, the practice of coating with magnetite has been adopted. This practice has made possible excellent converter campaigns, withstanding overblowing. Coatings are accomplished by blowing clean matte in the absence of silica. Without flux additions, the ferrous oxide may be further oxidized to magnetite, Fe_3O_4. This blow is continued until 2 or 3 in. of magnetite have been deposited along the tuyere line. When the coating has been applied, matte and fluxes are added and the normal slag blow commences. Whenever brick surfaces are exposed, it is necessary to renew this coating.

Matte, containing 40 to 45 pct copper, is tapped as needed by the converters, and flows down launders, covered with hoods to draw away gases, to ladles.

The most feared occurrence in converter operation is the failure of either air or power sources. Sudden air failures may cause tuyeres to be filled with molten material, and at critical stages of converting, a power failure may cause extensive damage to the lining. Either occurrence may result in extensive operating delay. Generally, there is sufficient forewarning of air failures to permit turning converters out of the blowing position before any damage is caused. On the other hand, power failures are sudden and unpredictable. To reduce this hazard, an emergency battery power system is maintained. Although incapable of supplying power to turn more than one converter at a time, each converter may be removed in sequence from the blowing position. The battery circuit also supplies emergency power to the blister holding furnaces.

Until recently, all electrical power, as well as all converter and high pressure air, was applied by Garfield's power dept. Even now, purchased power represents but a small fraction of plant requirements. Installed power generating equipment has a total capacity of 11,500 kw, of which 1500 kw are direct current for certain heavy equipment and electric haulage lines. Four turbo-blowers and three reciprocating blowers supply air for converter blast, and two compressors furnish high pressure air. About 65 pct of the steam requirements are generated by reverberatory waste heat boilers, and the balance by two direct fired boilers.

Although the smelter's location is favorable in relation to sources of raw materials and to rail facilities, the water supply is limited. Water is of two general categories. So-called fresh water having a hardness of about 80 ppm, and brackish water having a hardness of 540 ppm. Fresh water is used for domestic purposes around the plant, and, after suitable treatment, for boiler feed water. Brackish water is used in powerhouse condensers, for process cooling, and for fire protection. Because of the limited quantity of water in the area, plant waste water is reclaimed and used as process water in Kennecott's concentrators.

Fe-Ni-Co Alloys For

Glass to Metal Seals

by K. H. Mairs

MATCHING the thermal expansion characteristics of glass and metal is a problem that always has been faced by the vacuum tube industry. The earliest incandescent lamps contained lead-in wires of platinum because it was the only metal then available that permitted vacuum-tight seals to be made readily with certain soft glasses. The high cost of platinum led to the development of platinite, a 46 pct Ni-Fe alloy, having substantially the same expansion coefficient as platinum. Platinite was not entirely suitable and was soon replaced by Dumet, a composite wire having a core of 42 pct Ni-Fe alloy and a sheath of copper equal to 20 to 25 pct by weight of the whole. Dumet is still popular and is employed where small wire sizes are permissible. The practical maximum diameter of Dumet is limited to 1 mm by the entirely different radial and longitudinal expansion characteristics. Where larger wire sizes are necessary, as in power tubes, tungsten and molybdenum are used.

The Housekeeper seal, which allows any metal to be sealed to any glass regardless of expansion characteristics, provided only that they will stick together, is used primarily in power-tube manufacture. This seal usually is made between Pyrex glass and copper. It has certain marked disadvantages, such as mechanical weakness, susceptibility to amalgamation where mercury vapor is employed, and early failure by fatigue.

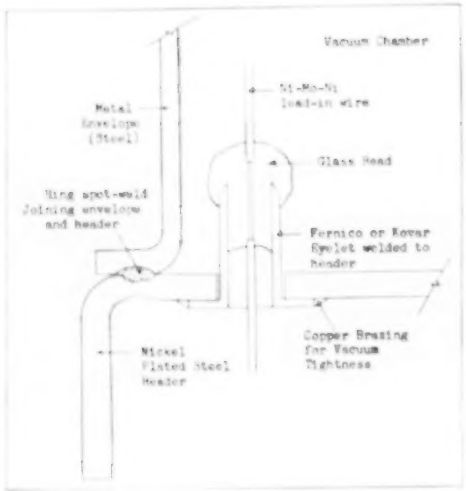
Other alloys have been developed for sealing to glass. Both European and American manufacturers have used 26 to 28 pct Cr-Fe alloys extensively and much attention has been given to a family of alloys of iron, nickel, and cobalt.

The expansion characteristics of Fe-Ni and Fe-Ni-Co alloys are unusual because they are not linear functions of temperature as are the expansions of most metals. These alloys have low expansivity at temperatures less than their characteristic inflection temperatures and considerably greater expansivity at higher temperatures. By proper compounding, the inflection temperature of Fe-Ni-Co materials can be made to coincide with the annealing range of certain glass compositions, and expansion properties can be made to match or approach those of the glasses.

The properties and behavior of Fe-Ni alloys of the Invar type are summarized by the Bureau of Standards. Brave[1] discovered that the addition of cobalt could be used to displace the inflection temperature to higher values and thereby extend the temperature range in which minimum expansivity could be utilized. Scott[2] made an extended study of the expansion characteristics of Fe-Ni-Co alloys, evaluating the influence of the principal ingredients and of the usual contaminants. His formulas for expressing expansion characteristics in terms of chemical composition are intended to apply to materials in which the A_3 crystallographic transformation is suppressed to at least −100 C. Later, Scott[3] credited the alloy Kovar as having the best match of expansion properties with several available glasses. Fernico discussed by Hull and Burger[4] has essentially the same composition and properties as Kovar. Miner and Seastone[5] commented upon Kovar when discussing typical problems in melting and annealing electrical alloys.

The appearance of the metal envelope vacuum tube in 1934 presented many problems in metal technology not encountered previously by the tube manufacturing industry. One problem was the utilization of the new Fe-Ni-Co expansion alloys in the mass production of low cost receiving tubes. While the usual glass envelope was replaced by a metal one, glass could not be eliminated completely. Glass was still used to insulate lead-in wires from the grounded envelope. The typical construction of an early metal tube is shown in Fig. 1. The header was a low carbon steel stamping, nickel plated so that metal oxides formed during the glass bead-making operation could be reduced in hydrogen at temperatures lower than the softening point of the glass. Eyelets of the Fe-Ni-Co alloy (Kovar or Fernico) were spotwelded and copper brazed to the header. Lead-in wires were usually nickel-molybdenum-nickel with molybdenum as the expansion element within the glass bead and nickel as both the supporting and positioning element within the vacuum

Fig. 1—A typical detail drawing of an early "all metal" vacuum tube


Vacuum Chamber
Ni-Mo-Ni lead-in wire
Metal Envelope (Steel)
Glass Bead
Ring spot-weld Joining envelope and header
Fernico or Kovar Eyelet welded to header
Copper Brazing for Vacuum Tightness
Nickel Plated Steel Header

K. H. MAIRS is Assistant Professor of Metallurgy at the University of Rhode Island, Kingston, R. I.

Table I. Chemical Composition of Fernico and Kovar

Material	Fe, Pct	Ni, Pct	Co, Pct	C, Pct	Mn, Pct
Kovar (nominal)	54	29	17		
Fernico (nominal)	54	28	18		
Fernico CG510	53.0	28.0	17.9	0.06	0.23
Fernico CG604	54.1	27.6	17.9	0.06	0.18

chamber and the means for making electrical contact with the base pins. Kovar or Fernico was rarely included as a portion of the lead-in wire (replacing molybdenum), although some such lead wires were made and tried experimentally with good results.

Measurement of total expansion and calculation of expansion coefficients were made on each heat of alloy strip and on most lots of fabricated eyelets. A strip approximately 1 in. wide was rolled into a tube about $\frac{1}{4}$ in. diam x 4 in. long. It was then tested in an ordinary dilatometer, which indicated the differential expansion between the specimen and a fused silica tube on a dial gage sensitive to 0.0001 in. These data were then converted into true unit expansion. To insure uniform temperature along the test specimen, the bottom 6 in. of the silica tube was jacketed with a massive copper sleeve. At first, expansion measurements were made from room temperature to approximately 600 C. It soon was recognized that the temperature at which Ar$_1$ transformation took place also must be determined. To make this test, liquid air was poured into the furnace chamber so that it contacted the copper sleeve.

Expansion measurements on fabricated eyelets were taken with an interferometer using helium radiation of $\lambda = 5875$A. Three eyelets, honed to uniform length (within a few wave lengths of light), were used to separate quartz optical wedges. The passage of interference fringes past a hairline in the viewing eyepiece was a measure of the eyelet length change. This information could be used to plot total expansion and to calculate coefficients. This test method was particularly useful for demonstrating the comparative performance of three metal specimens simultaneously. Rotation of the interference pattern would indicate that the specimens were expanding at different rates. It was impractical to use the interferometer at temperatures lower than room temperature. Within its useful temperature range, the interferometer gave expansion data directly equivalent to the dilatometer.

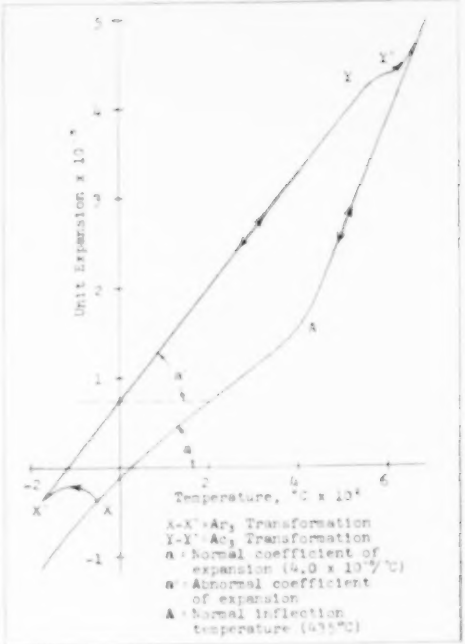

Unit Expansion x 10 ⁴
Temperature, °C x 10²
X-X' = Ar₁ Transformation
Y-Y' = Ac₁ Transformation
n = Normal coefficient of expansion (4.0 x 10⁻⁶/°C)
n' = Abnormal coefficient of expansion
A = Normal inflection temperature (435°C)

Fig. 2—The typical expansion curve for Fernico or Kovar is shown. The lower curve, through X and A, depicts normal expansion. Abnormal expansion follows the curve X X' Y Y' A.

Nominal compositions of Kovar and Fernico are noted in Table I. Both are normally reversible alloys with inflection or transition temperatures in the neighborhood of 435 C and expansivities between 25° and 325 C of approximately 4.0 x 10^{-6} per °C. Above the inflection temperature the expansivity may be as much as 12.0 x 10^{-6} per °C. A plot of the normal and abnormal characteristic expansion of Fernico or Kovar would be similar to that shown in Fig. 2. The normal expansion follows the lower curve of the figure only.

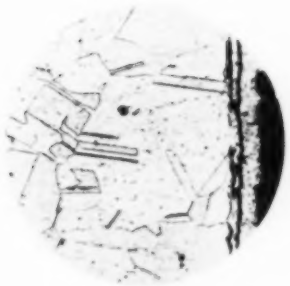


Fig. 3—Normal Fernico, annealed 10 min at 1000 C in H. Etched with aqua regia and CuCl. X500.

Fig. 4—Normal Kovar, annealed 10 min at 1000 C in H. Etched with aqua regia and CuCl. X500.

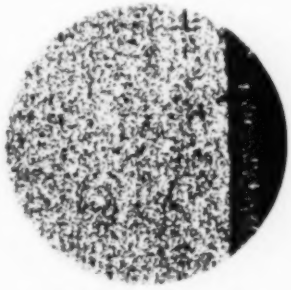


Fig. 5—Cold formed Kovar eyelet, extremely fine grain fragments. Etched with aqua regia and CuCl. X500.

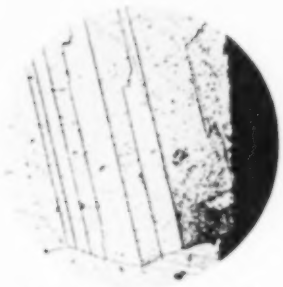


Fig. 6—Extremely coarse grained Kovar eyelet, annealing treatment unknown. Etched with aqua regia and CuCl. X500

Fig. 7—Kovar eyelet, abnormal after chilling to −80° C. Etched with aqua regia and CuCl. X200

Fig. 8—Kovar eyelet, abnormal with high coefficient of expansion. Etched with 10 pct nital. X200

The normal metallographic structure of both alloys in the annealed condition is that ordinarily observed for face-centered cubic materials. Typical microstructures of normal annealed and cold worked materials are shown in Figs. 3 to 6. In their normal condition these alloys are difficult to etch. One suitable etchant is freshly prepared aqua regia saturated with cupric chloride. It is best to rub the metal surface gently over a soft cloth moistened with the etchant.

At room temperature and all temperatures below the inflection point, normal Kovar and Fernico are ferromagnetic; above the inflection point they are essentially nonmagnetic. It is commonly accepted that the abrupt change in expansion coefficients of Fe-Ni and Fe-Ni-Co alloys at the inflection temperature is associated with the A$_2$ magnetic transformation. The hardness of annealed normal Kovar or Fernico is approximately 70 to 80 R$_B$.

It occasionally was observed that glass beads within the Kovar or Fernico eyelets, although well formed, were cracked so as to suggest that the glass and metal had radically different expansions. Metallographic examination revealed an abnormal microstructure such as might be expected if the A$_2$ transformation had started during cooling to room temperature, or at some point not far below room temperature but well above −100° C. The microstructure of an abnormal eyelet is shown in Fig. 7. Ordinary 10 pct nital can be used to etch abnormal materials, as shown in Fig. 8. Its similarity to the appearance of martensite in alloy steel is responsible for the normal and abnormal structures being referred to as austenite and martensite respectively.

A search of available strip stocks for a material with abnormal microstructure was not immediately fruitful. It was for this reason that expansion measurements below room temperatures were begun. Annealed specimens of many heats of material experienced A$_2$ transformations between −40° and −60° C. The transformation was accompanied by a marked volume expansion and an increase in hardness to about 90 to 100 R$_B$. It was apparent that Rockwell hardness vs cold treating could be used as a means for rapid survey, and that selected materials could then be examined more critically with the dilatometer. It became common practice to measure the hardness of annealed material at room temperature (+25° C), to measure it again at room temperature after placing the specimen in intimate contact with solid carbon dioxide (−80° C), and measure hardness still a third time at room temperature after immersing the specimen in liquid air (−180° C). If an appreciable increase in hardness was noted between +25° and −80° C the material was subjected to further examination. If an increase in hardness was first noted between −80° and −180° C, the material was considered normal and suitable for tube making, providing that its expansion performance was satisfactory. Many materials were completely unaffected by cold treatment to −180° C, and these too were considered suitable for their intended purpose. Table II illustrates typical hardness vs cold treating data.

Table II. Rockwell B Hardness vs Cold Treating

Material	Rockwell B Hardness at +25° C		
	Annealed	Chilled to −80° C	Chilled to −180° C
Kovar N	73.0	73.0	89.0
Kovar A	81	82	101
Kovar B	86	94	102
Fernico 1	70	70	77
Kovar Y	74.5	74.5	91.5
Fernico 1 (Duplicate)	74.0	74.0	91.5

Materials in which microstructure was made abnormal by cold treating thereafter exhibited abnormal expansion as shown diagrammatically in Fig. 2. The material was no longer a reversible alloy, but distinctly irreversible. The A$_2$ transformation, starting at X and essentially complete at X'', was dependent upon composition and to some extent upon prior treatment. The expansion caused by heating was abnormally rapid until some temperature range Y-Y'' when the A$_2$ reaction took place and the material reverted to its normal structure and expansion characteristics.

Eventually a metal sample, Fernico CG518 in Table I, was found in which the A$_2$ transformation occurred near room temperature (0° to −10° C). Once transformed, this alloy would, of course, show abnormal expansion; chilling to −180° C in liquid air was unnecessary.

Because normal Kovar or Fernico had lost its magnetism when heated to approximately 500° C and the A$_2$ transformation in abnormal materials had not yet taken place at that temperature, mixed eyelets were occasionally separated at that temperature by removing as abnormal all those which were magnetic. This method of separation was quite sensitive and reliable.

Fig. 9—Fernico CG518 strip, cold rolled 50 pct of thickness to 0.0065 in. Etched with aqua regia and CuCl. X600.

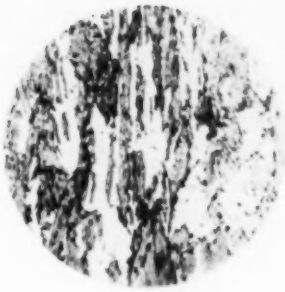


Fig. 10—Fernico CG518 strip, cold rolled, annealed 1 hr at 500° C in H. Etched with aqua regia and CuCl. X600.

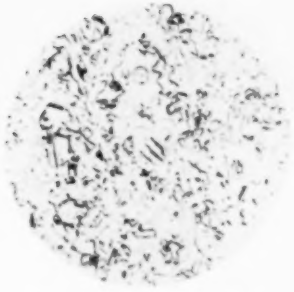


Fig. 11—Fernico CG518 strip, cold rolled, annealed 1 hr at 700° C in H. Etched with aqua regia and CuCl. X600.

Attempts to explain the observed abnormal behavior of Kovar and Fernico by analytical chemical methods alone were not successful. The difficulty in separating nickel and cobalt left the results open to question. Analyses were made only for nickel, cobalt, carbon, and manganese, and the difference was reported as iron. It is suspected that the presence of even small quantities of other metals, particularly chromium, might markedly influence the behaviot of these alloys. The many analyses did show the constancy of manganese content, however. In practically all examinations manganese was in the range 0.15 to 0.30 pct. Carbon content was within the range 0.04 to 0.06 pct. This concentration was not unusual since these materials are annealed in wet hydrogen to decarburize to a maximum extent.

The analytical data suggested that abnormality could be corrected by increasing the carbon content moderately. This was done many times by annealing the expansion materials in hydrogen passed over, or bubbled through, almost any hydrocarbon having a reasonable vapor pressure at room temperature. However, the added carbon was neither easily controlled nor evenly distributed and sealing to glass almost invariably resulted in the formation of many tiny gas bubbles. Homogenizing to allow carbon diffusion often resulted in decarburization. Carburizing thus restored expansion and structural characteristics to abnormal material but did not yield a material of suitable quality for sealing to glass.

The influence of mechanical working upon abnormality was investigated by subjecting the material showing A_r transformation in the range 0° to −10° C (Fernico CG518), to 50 pct reduction in thickness by cold rolling at room temperature. The as-rolled structure is shown in Fig. 9. To demonstrate the presence of martensite produced by mechanical working, specimens were heated in hydrogen for 1 hr at increasing temperatures beginning at 300° C. Fig. 10 shows tempered martensite, the dark constituent, mixed with untransformed austenite.

Cold rolled specimens heated to temperatures not exceeding 600° C, if subsequently chilled in liquid air, did not thereby experience change in microstructure or hardness. Heating to 700° C allowed the A_r transformation to take place as shown in Fig. 11. This photomicrograph shows a completely recrystallized fine-grained austenite; there is no obvious abnormality. If, however, specimens heated to 700° C or more were then chilled in liquid air, the abnormal microstructure reappeared as shown in Fig. 12. Martensite shown in the bottom half of this micrograph is revealed by surface distortion resulting from the volume expansion accompanying the A_r transformation.

This particular lot of cold worked expansion alloy developed a peculiar type of microstructure when annealed at temperatures greater than 700° C. The development of a leaf-like constituent with distinct mid-ribs and the appearance of a two-phase structure is shown in Fig. 13. It is believed that increasing grain size resulting from the higher annealing temperatures has permitted the A_r transformation to begin above room temperature, and this structure consists of large martensite needles in a partially transformed austenite. Another lot of similar ma-

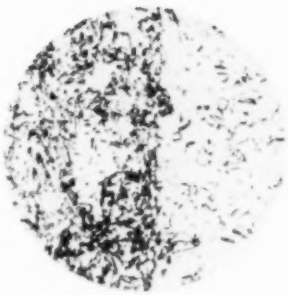


Fig. 12 (Left)—Fernico CG518 strip, cold rolled, annealed 1 hr at 700° C in H. Etched with aqua regia and CuCl, then chilled in liquid air. No additional etching. X600.

Fig. 13 (Right)—Fernico CG518 strip, cold rolled, annealed 1 hr at 1000° C in H. Etched with aqua regia and CuCl. X600.

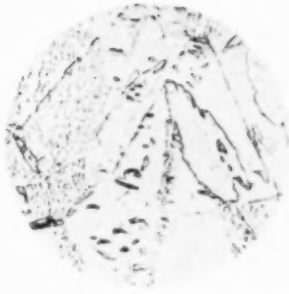
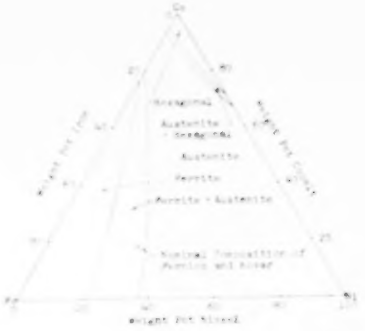


Fig. 14—Left—The microstructure of Fe-Ni-Co alloys furnace cooled to room temperature from the melt. (Kase.)

Fig. 15—Right—Equilibrium diagram of the Fe-Ni-Co system (projection on the basal plane) at 200° C. (Kase.)



terial made extremely coarse grained by prolonged annealing at 1100° C. was completely martensitic after cooling to room temperature. The A_3 transformation was not determined but had occurred during the cooling process.

Most lots of Fernico and Kovar had A_3 transformation normally well below room temperature (−80° to −180° C). Cold working these lots at room temperature to 50 pct reduction in thickness caused only grain fragmentation and produced no evidence of A_3 transformation. Expansion characteristics after cold working were normal, and recrystallization took place in the range 600° to 700° C. Grain growth took place on heating to higher temperatures. Grain size was large at 1000° C. and very coarse at 1100° C.

The following conclusions may be drawn:

1—The type of equilibrium diagram proposed by Kase, Figs. 14 and 15, is probably essentially correct. It is doubtful that his materials were examined under equilibrium conditions and the location of phase boundaries is therefore open to some question. Nevertheless, this is a satisfactory key for explaining the general behavior of Fe-Ni-Co alloys.

2—The formulas proposed by Scott[7] for selecting alloy compositions in which A_3 transformations are suppressed to −100° C. are not entirely satisfactory because they do not recognize important physical factors such as mechanical stress and grain size.

3—The comments of Scott upon the influence of carbon in stabilizing the structure of these alloy compositions has been demonstrated experimentally many times. The presence of carbon in these alloys where used for sealing to or through glass cannot be tolerated, however, because of reactions between carbon and the various oxides in glass. Glass bubbles are formed at the metal-glass interface, reducing mechanical strength and destroying vacuum tightness. Expansion alloys for sealing to glass must be essentially carbon free.

4—Work hardening has an appreciable influence on the temperature at which A_3 transformation takes place. An annealed material which on cooling experienced A_3 transformation between 0° and 10° C. was transformed 50 pct or more to martensite by plastic deformation at room temperature.

5—Grain size apparently has an appreciable influence upon the temperature of A_3 transformation in these Fe-Ni-Co expansion alloys. Some materials, annealed at high temperatures and thereby made very coarse grained, experienced A_3 transformation above room temperature during the cooling process. In some compositions, the temperature of A_3 transformation may rise with increasing grain size.

6—Recrystallization takes place in the temperature range of 600° to 700° C. producing a fine grained material of normal structure. Grain growth takes place rapidly at higher temperatures.

7—Normal properties are to be expected of Fe-Ni-Co expansion alloys which are entirely austenitic and do not experience crystallographic transformation. Abnormal microstructure, expansion characteristics, or magnetic properties indicate a material which has experienced some transformation to martensite. In this latter form it is distinctly irreversible and unsuited for its intended use.

Fernico, Kovar and allied compositions for glass-to-metal seals are commercially useful materials because of their practical as well as their theoretical behavior. Their chemical compositions and thermal and mechanical processing are such that the resulting materials are intended to be reversible and have expansion characteristics suitable for matching the expansion of certain glasses. These alloys are probably often used under non-equilibrium conditions and a number of factors, singly or in combination, may favor crystallographic transformation. If this transformation should take place, the expansion characteristics of the alloy become irreversible, the properties in general become abnormal and the material is not suitable for its intended use.

Wyman[8] has confirmed the argument that factors other than chemical composition have influence upon the temperature of A_3 transformations in Fe-Ni-Co alloys. Along with other items he discusses the influence of grain size and stress. Kramer and Walters[9] have reported that transformation of the normal austenitic structure to a mechanical mixture can take place at 480° C. if sufficient time is allowed for the reactions. These researches suggest that under true equilibrium conditions A_3 and A_1 may occur at the same temperature.

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Open Hearth Rebuild Program *Increases* Furnace Availability

by J. L. Walton and J. O. Dague

INTENSIVE planning and scheduling of a rebuilding program was started late in 1950 at the Lackawanna plant of Bethlehem Steel Co. to squeeze more tonnage out of existing furnaces. Furnace availability in 1950 was 93.4 pct, and in 1951 increased to 95.8 pct. In tonnage, 1951 open hearth production was over 4 million tons compared to 3.6 million tons in 1950. While the greater availability of the furnaces only can be credited for part of this increase in production reviewing and improving the details of operation to get more uniform campaign life, resulted in many other improvements in operation.

The job of long range scheduling of rebuilds requires a knowledge of the number of heats per campaign. The better this is known, the better the long range schedule that may be set up. This problem is somewhat difficult at the Lackawanna plant because of the many types of furnaces involved. There are 30 furnaces in the plant, with four more being built. The first were built in 1906 and the last in 1936, and they include the various ideas of furnace construction from the beginning of the century to the present.

Furnaces are arranged in three shops, No. 1 shop has 14 furnaces, all tapping 147-ton heats. Six of these furnaces are small, having a hearth area of 648 sq ft, and eight have a hearth area of 708 sq ft. The checkers are all single pass.

No. 2 shop has 10 furnaces. Two furnaces tap 290-ton heats into two ladles per heat, and eight furnaces tap 150-ton heats. The hearth areas of the two big furnaces are 792 sq ft and 910 sq ft. The other eight furnaces are 730 sq ft. All furnaces are double-pass except three of the small ones.

No. 3 shop has six furnaces tapping 220-ton heats. Each has a hearth area of 867 sq ft and all have double-pass checkers. Four new furnaces of the same design as the present ones are being built.

Based upon past results and estimates of present performance, a rebuild schedule is planned for two months ahead. On this schedule, the condition the furnaces will be in at the end of that time is shown. This schedule is not and cannot be an inflexible one. However, making 72 heats per day and averaging 216 heats per campaign, it is necessary to rebuild a furnace every three days. Because of differences in the construction and operation of each of the 30 furnaces, the same length of campaign is not planned for all of them.

In 1950, No. 1 shop averaged 218 heats per campaign, in 1951 241 heats, and rebuilds are currently scheduled for 250 heats. This increase in campaign life was not achieved at the expense of production; production rose from 13.0 tons per operating hr in 1950 to 13.6 tons in 1951. Currently the shop is operating at 14.0 tons per hr.

No. 2 shop in 1950 averaged 211 heats per campaign; in 1951 the average was 255 heats. Production was also increased, from 13.3 tons per hr to 14.7. The two 290-ton furnaces averaged 142 heats per campaign in 1950 and 152 in 1951. Tons per hr increased from 20.6 tons in 1950 to 23.2 tons in 1951.

No. 3 shop campaign life in 1950 and 1951 was the same, 150 heats. However, the tons per hr increased from 20.7 to 22.2. Work is in progress on getting the campaign life for the large furnaces up to 250 heats, which will simplify scheduling.

Even after the scheduling of the rebuilding program is completed, the day-to-day problems of operating the furnaces and planning of which furnace to take off must continue. The condition of the furnaces is gone over carefully by the bricklayer foremen and the shop superintendent. Often it is advantageous to juggle the schedule because one furnace is in a better condition than another. Other times, a furnace may have to be hot patched to keep it on when it should be rebuilt. Sometimes a furnace that will run and make steel for many more heats is rebuilt. The hardest decision is to take a furnace down that still is good for a week or two more. Attempts are made to keep such fluctuations to a minimum. Every week the rebuild meeting is attended by the open hearth superintendent, the assistant superintendent of the mechanical dept., bricklayer foremen, mechanical foreman, carpenter foreman, combustion engineers, refractories engineer, and others concerned with rebuilding. The results of the previous week's rebuilding are studied, and the schedule for the coming week planned.

The operation resulted in longer campaign life and 10 pct greater tonnage from the furnaces. There is no easy road, or secret formula for getting more tons per year from a furnace and it was necessary to consider every fundamental factor. Blast furnaces helped tremendously by giving a more uniform iron, with lower silicon content. The average silicon content dropped from 1.08 pct in 1950 to 0.95 pct in 1951. Charging time was reduced by an average of 20 min per heat. (Hot metal percentage was the same). Firing rates and combustion practices on the furnaces were followed carefully. Furnaces were sealed better to prevent air infiltration. The checkers and flues were kept cleaner. The morale of the foremen and

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This paper was presented at the National Open Hearth Steel Conference, Pittsburgh, Mar. 31, 1952.

Fig. 1—Drilling of the 10 ft high slag; the furnace was tapped 4 am the following morning.

Fig. 2—At 7:30 am, the furnace was cooled, and the bulkhead knocked in.

the men has been excellent, and this is an important prerequisite to maximum production.

The mechanical dept. in the plant deserves credit for the outstanding job done. Rebuilding time is figured from the oil off to completed rebuild (when the last bulkhead is closed). In 1950 the average time was 131 hr and in 1951 it was 94 hr. In 1952 this average will be even lower because they are now rebuilding furnaces in 72 hr or less. They are rebuilding more furnaces now than formerly because, even though campaign life has increased, an average heat time is between ½ and 1 hr shorter, resulting in shorter campaigns.

The scheduling of open hearth repair work is based on all furnaces being inherently the same. There are differences in sizes and details of engineering and construction, but the important components are similar. The repair work on these similar furnaces differs in extent. One furnace may be torn down further than another and may necessitate more replacement brick. However, the sequence of operations can and should be exactly the same.

This being conceded, the decision was made to standardize all operations in repair work. In short, to mass produce furnaces. To accomplish this aim, all rebuilds are performed according to a rigid, written schedule. The schedule covers every detailed operation of a repair job, from the time the furnace is tapped to the time the fuel is turned on the furnace. Each operation has been segregated, analyzed, and timed down to the minute. A standard sequence of operation has been adopted. The correct number of men to perform any operation in the alloted time is detailed.

The entire rebuild is scheduled so that each operation will occur at the best time of day to suit local conditions. For example, the roof is always installed at 10 am, when the maximum number of men and supervision is available. Similarly, slag is always disposed of on the day turn.

These written schedules are of three types: Floor level, with or without slopes and carrying arches; complete pit level; and quick roof. Checker work is done on a separate schedule that is synchronized with the furnace schedule. Only once in the past nine months has the furnace light-up been delayed because of work on the checkers.

Having condensed rebuilding to three standard types, only sufficient information is required to determine the type of rebuild any given furnace is expected to receive. This is determined from knowledge of the condition of the furnace at the end of the last rebuild, and the information given by the open hearth personnel on service during the last campaign.

Special information, such as *break-throughs*,

Fig. 3—At 5:45 am, the slag is in small chunks after shooting.

Fig. 4—At 9:15 am, the slag is shown being loaded on a bulldozer.

Fig. 5—At 12:00 noon, less than 8 hr after tapping, the slag pocket is cleaned out.

Fig. 6—Conveyor arrangement used for delivering brick to ends of a furnace when floor space is limited.

where it may be expected to find steel, plugged checkers, checkers that have operated at elevated temperatures, and any mechanical work, is furnished to the mechanical department on written form by the open hearth supervision.

Rigid scheduling of furnace rebuilds permits no delay, from any source. It calls for the utmost cooperation between the open hearth and mechanical departments as well as cooperation between crafts. The service the open hearth furnishes must be timed correctly.

For example, the open hearth departments know that a furnace to be rebuilt should be tapped between 2 and 5 am. Similarly, they know that they should have the cars of roof brick in front of the furnace at 10 am the following morning.

The open hearth personnel has copies of the schedule and knows precisely when to furnish crane service. This makes it easier to plan the operations ahead of time so that a crane is available when needed.

To cut this open hearth service to a minimum, the rebuild schedule calls for as little crane service as possible. By becoming more independent of open hearth service, the rebuild time can be controlled better. To this end, and for speed, slag is not *pulled*, but shot and loaded directly on trucks by bulldozer.

Fig. 1 shows the drilling of a 10-ft high slag, the day before furnace was to be rebuilt. The furnace was tapped at 4 am the following morning. Fig. 2 shows the furnace cooled and the bulkhead knocked in at 7:30 am. Fig. 3, taken at 8:45 am, shows the slag in small chunks after shooting. Fig. 4, taken at 9:15 am, shows the bulldozer loading slag. Fig. 5, taken at 12:00 noon, shows the slag pocket cleaned out, less than 8 hr after tap.

All brick is delivered to pit by truck and unloaded and placed by pallet machine. Pit crane service is negligible. Similar planning has reduced crane demand on the floor. In No. 3 shop, all brick is delivered by car or pallet machine. In No. 2 shop, all brick is delivered by car. In No. 1 shop, where floor space is limited, brick is delivered by truck and pallet machine to the pit and conveyed to the ends of the furnace. Fig. 6 shows the arrangement of these conveyors.

To the mechanical dept. scheduling means elimination of confusion and interference, and pin-pointing of trouble. The time taken on any operation is entered in the schedule form adjacent to the standard time allowed. This is done by the foreman in charge of the operation.

If there are any deviations from standard, they are investigated at the weekly craft meeting, and steps are taken to prevent their recurrence. This meeting is attended only by the carpenter, bricklayer, labor, millwright, materials handling foreman, and the assistant superintendent of the mechanical dept. Here the techniques and problems of furnace rebuilding are discussed and planned. This is the group that makes and alters the schedules to suit improved practices.

Rigid scheduling removes the guesswork, interference between crafts, and interference between repairs and operation of furnaces. The craftsmen earn more money, the supervisors' duties are much lighter, and furnace availability is greater, because of the resulting shorter rebuild time.

Fig. 7 gives the entire story. It shows the comparison of furnace down-time to brick laid per bricklayer man hr for the period of converting to scheduled rebuilds. The dotted line shows the lowering of down-time per furnace. The solid line shows the increase in efficiency of brick laid during the same period, attributed to correct scheduling and planning. The efficiency of the rebuild has increased in direct proportion to the decrease in down-time.

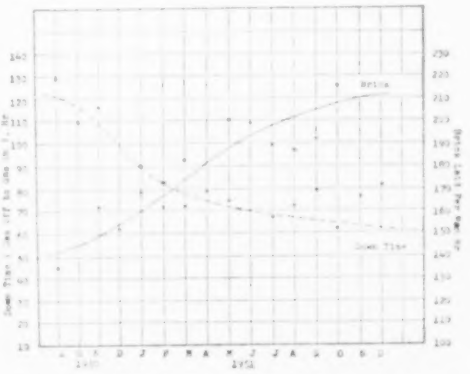

Fig. 7—The graph shows the increase in efficiency of brick laid, and the lowering of down time per furnace, resulting from the rebuilding program.

Manganese for the Steel Industry

by F. W. Boulger and R. C. Buehl

THE steel industry currently uses about 700,000 tons of manganese annually. Technically feasible changes in composition probably would not lower the manganese content of finished steel by more than 5 pct. Furthermore, it is too inexpensive and useful an element to justify even this much substitution. Therefore, the assurance of an adequate supply of manganese is of vital importance to the nation as well as to the steel industry.

Among other reasons, manganese is added to steel to improve its hot working properties. C. T. Anderson and coworkers of the Bureau of Mines made iron-carbon alloys containing only 0.004 pct Mn and tested them by twisting at hot rolling temperatures. They found it necessary to reduce the sulphur content to 0.002 pct to obtain good hot working properties. In these experiments, iron-carbon alloys with only 0.004 pct Mn could not be forged if the sulphur content exceeded 0.017 pct.

Even though there is no current shortage of manganese, the problem of making the United States relatively independent of foreign supplies is receiving attention. Studies are in progress on recovering manganese from low grade American ores and from open hearth slags. Slags are a potential source of manganese as Vignos¹ showed in 1949. At present, more manganese goes to slag dumps than is received by steel plants as a ferroalloy.

R. C. Buehl and M. B. Royer described the Bureau of Mines pyrometallurgical process for recovering manganese from open hearth slag. This two-stage process involves producing spiegeleisen from open hearth slag in a blast furnace and then oxidizing it in a basic converter to obtain a high manganese slag.

A three-ton per day experimental blast furnace was operated by the Bureau of Mines during a period of several months. With this small experimental furnace, a spiegel containing 21 to 23 pct Mn, 0.8 to 1.0 pct Si, and 3 to 4 pct P was produced from open hearth flush slag in a run covering several days. During this period, the manganese content of the slag varied from 3 to 4 pct. Tests also were run with a higher-iron flush slag, a mixture of flush and tap slags, and a manganiferous Maine ore. These raw materials resulted in spiegel of somewhat lower manganese content. Recoveries of around 60 pct were obtained in all the tests without the reuse of flue dust, which contained from 6 to 13 pct of the manganese charged. Coke consumption ranged from 3300 to 4100 lb per ton of spiegel depending on the charge. High furnace temperatures and consequently slags of low manganese content were obtained by the use of high hot blast temperatures ranging from 1800 to 2200 F. Heat losses from a small furnace are proportionately very high, so from the standpoint of thermal balance a commercial furnace should theoretically be able to obtain comparable results at blast temperatures around 500 F lower. However, it has been demonstrated that good results could be obtained at lower temperatures.

In the second stage of the process, the spiegel containing 3 to 4 pct P was preferentially oxidized to give a manganese-rich slag low in phosphorus. Experiments in a basic lined, 500-lb converter indicated that single-stage treatments were unsatisfactory. Although manganese recoveries were good, the slags contained about 52 pct Mn, 10 pct Fe, and 0.8 pct P. Therefore, this product did not have the manganese to iron and phosphorus ratios exceeding 8 and 250 to 1, respectively, desired by ferroalloy producers.

Royer and Buehl found, however, that cyclic treatments would produce high-manganese slags with consistently low iron and phosphorus contents. The cycle recommended consists of: 1—Oxidizing the spiegel to 1 pct Mn, and tapping the metal and retaining the slag; 2—Adding and partially blowing fresh spiegel, tapping the slag and retaining the metal, blowing the metal to 1 pct Mn and repeating the cycle. Such cyclic operations recovered about four fifths of the manganese from spiegel containing 3 to 4 pct P, 2 to 3 pct Si, and 20 pct Mn. The slag product contained approximately 50 pct Mn, 2.0 pct Fe, 0.08 pct P, and 22 pct SiO. Unfortunately, there are objections to such high silica contents.

Laboratory tests indicated that using spiegel with lower silicon contents would produce a viscous slag containing about 13 pct SiO. These slags trap about one tenth their weight of high-phosphorus metal shot. Magnetic separation of slags crushed to −20 mesh gave manganese recoveries of 98 pct. The final product contained about 60 pct Mn, 2.8 pct Fe, 0.15 pct P, and 15 pct SiO. The composition of this material is closer to the current silica specifications for manganese ores. The Mn to phosphorus and Mn to iron ratios are satisfactory.

In any pyrometallurgical recovery process, which involves the reduction of manganese, a low ratio of the MnO content of the slag to the manganese in the metal is important in obtaining an acceptable manganese recovery from low grade raw materials.

Stukel and Cocubinsky studied the distribution of manganese between slag and metal using a graphite crucible in an induction furnace. Their results showed that at constant reaction temperature, MnO in the slag is proportional to the manganese content of the metal over the range normally found in basic pig iron (1 to 4 pct Mn). The ratio of MnO in the slag to Mn in the metal decreased with increases of lime-silica ratio, but the rate of decrease was rather small at basicities above 0.9. Magnesia can be substituted for lime up to 13 wt pct without affecting the manganese distribution. The alumina content of the slag did not appear to affect the manganese distribution. The manganese recovery was enhanced by high lime-silica ratios, high temperatures, and low slag volumes.

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F. W. BOULGER is Supervising Metallurgist, Battelle Memorial Institute, Columbus, and R. C. BUEHL is Chief, Ferrous Pyrometallurgy Section, Bureau of Mines, Pittsburgh. This session held on Tuesday afternoon, Feb. 19, 1952 at the AIME Annual Meeting, was sponsored jointly by the Extractive Metallurgy Div. and the Iron & Steel Div.

Chromium Carbide in Stainless Steel

by A. B. Kinzel

IT is with sincere appreciation and a deep sense of responsibility that I accept the honor of delivering the Howe Memorial Lecture. In our time metallurgical research has delved into phenomena ever more complex in character, so that much of this work must be done by organized teams. We, of the Union Carbide and Carbon Research Laboratories and the Electro Metallurgical Co., are truly a team and the lecture which is to follow is due largely to a few of the outstanding members of that team here cited and well known to you in their own right: John Lamont, whose work deserves special recognition, Walter Crafts, William Forgeng, William Binder, Robert Fowler, and David Swan. Thus it is a fitting pleasure to accept this honor for the research institution which I represent.

Henry Marion Howe was truly inspirational and his breadth of view was such that he could use either the method of rigid proof or implied mechanism to further the broad understanding. But perhaps his outstanding characteristic was his sound judgment and his ability to weigh observations. The following is replete with observations and judgment as to their implication. We would like to feel that it is the type of dissertation which Howe, himself, would have enjoyed.

Chromium carbides in stainless steel have, in a sense, been a key to the progress of the stainless steel industry. Brearley's first stainless steel, containing approximately 0.30 pct C, was successful because it differed from previous Fe-Cr alloys in that the carbides were present in such amount and form as to provide the stainless and cutting properties. Again, the 12 pct Cr die steels with a carbon content of 1.5 pct or more achieved their properties by virtue of the form and distribution of the chromium carbides. In the straight chromium steels with from 12 to 25 pct Cr, chromium carbide amount and distribution are once more the determinants with respect to physical properties and corrosion resistance. In each of the cases just cited the role of the carbide is in essence similar to that of iron carbide in carbon steel and this story is so well known that we need not dwell on it.

In the austenitic stainless steels, the chromium carbide plays only a minor positive role with respect to mechanical properties, and for corrosion resistance the objective is to achieve maximum homogeneity. Thus the tendency has been to ever lower the carbon and correlatively the chromium carbide content of the austenitic steels. Today stainless steels with carbon less than 0.03 pct are beginning to find their true place, and this is being aided in major degree by our Company's introduction of a new type of ferrochromium having negligible carbon.

The role of carbon in these austenitic steels has long been recognized, and a truly enormous amount of research has been devoted to the subject. Much has been learned about corrosion resistance, but the attack on the problem from the point of view of carbide precipitation and the nature thereof has left much to be understood. Because of its fundamental importance to the future of stainless steels, further study of the mechanism of carbide formation in austenitic steels is of interest.

In the 18-8 Cr-Ni steels, which are typical of the austenitic class of steel, carbon is soluble in the austenite to the extent of approximately 0.15 pct at 1832°F (1000°C). The solubility becomes less with decreasing temperature, so that at 1652°F (900°C) the solubility limit is approximately 0.06 pct, at 1472°F (800°C) it is about 0.03 pct, and at 932°F (500°C) it is approximately 0.01 pct. Obviously this is the ideal situation for the classical precipitation phenomenon. It is true that, in a sense, 18-8 austenite resulting from annealing is in a metastable state, and the phenomenon of ferritic precipitation from this austenite should be considered. However, in a so-called fully austenitic 18-8 steel this is secondary with respect to the carbides and can be neglected. A wide variety of chromium carbides is known. Only one chromium carbide, Cr_3C_2, frequently referred to as Cr_4C, has been found in unmodified low carbon 18-8 steel. This, fortunately, simplifies the study of the precipitation phenomena.

For this study an A.I.S.I. type 304 stainless steel of commercial quality was selected. Analysis showed C 0.07 pct, Mn 0.49 pct, Si 0.33 pct, Ni 9.34 pct, Cr 18.91 pct, and N 0.033 pct. As expected with this composition the steel was homogeneous after annealing except for a few pools of ferrite, which were disregarded in that their location was not coincident with subsequent carbide precipitation areas. On corrosion testing the steel was normal and typical of good commercial quality.

Specimens $\frac{1}{2}$x1x4 in. were annealed and subjected to precipitation heat treatment for 100 hr at 100° temperature intervals from 1000° to 1500°F and for ten selected intervals ranging from 5 min to 64 hr at 1300°F. These blocks were then cut into small pieces for metallographic studies. The first problem

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TP 3307C. Manuscript, Feb. 21, 1952. New York Meeting, February 1952.

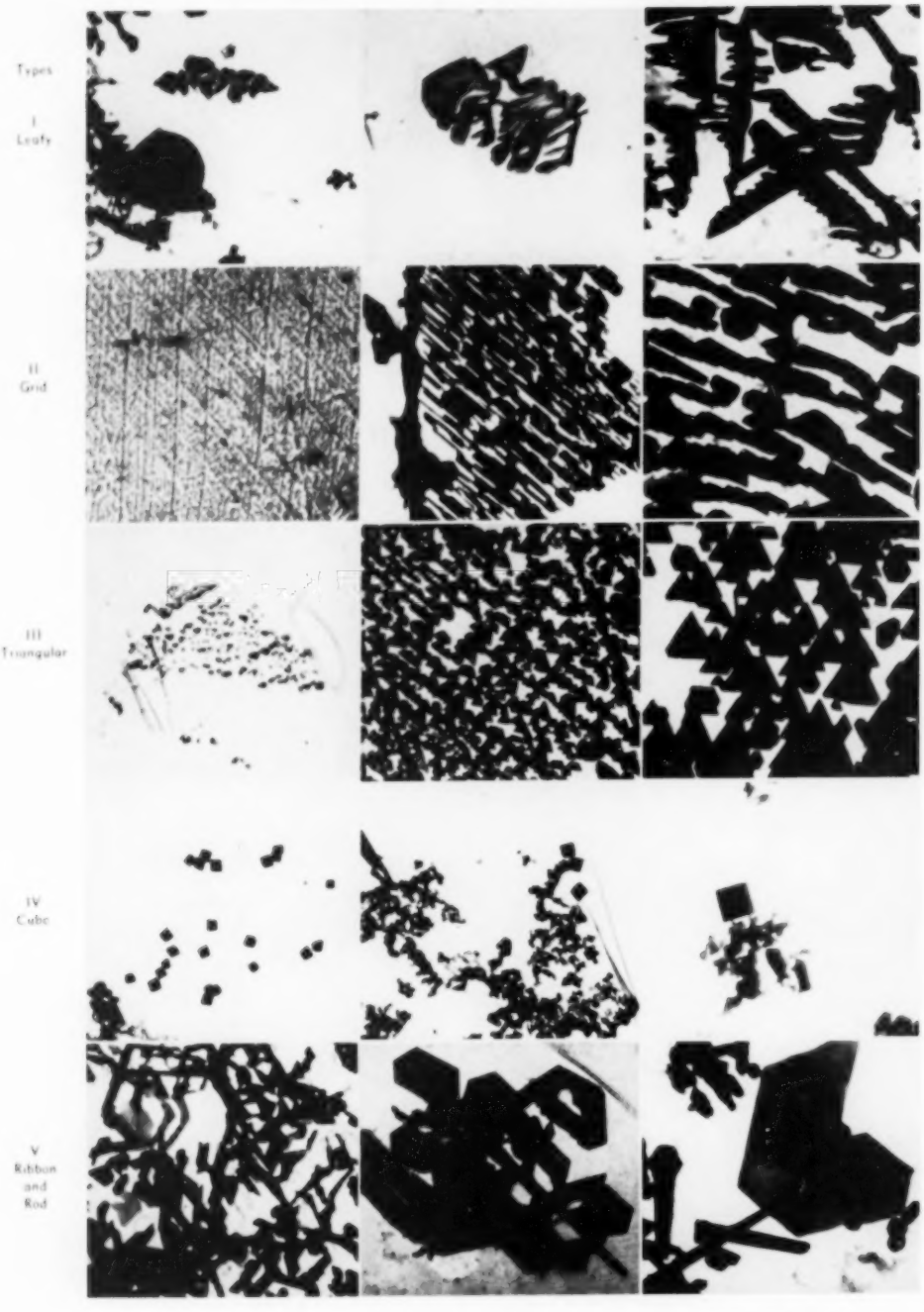
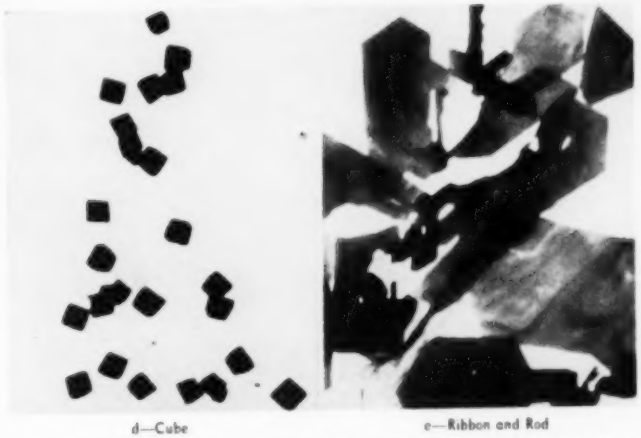


Fig. 1—Chromium carbide types after heating 100 hr at 100° intervals between 1000° and 1600° F. X10,000

a—Leafy b—Grid c—Triangular



d—Cube e—Ribbon and Rod

Fig. 2—Typical chromium carbide types after heating between 1000° and 1600° F. X20,000

was to study the form of the carbides proper, particularly in relation to their mode and locale of precipitation. To do this extractions were made and studied with the X-ray and the electron microscope, and samples of the metal proper and replicas of their surfaces were prepared and studied with the optical and the electron microscopes. As the resulting observations might be influenced by the method of sample preparation this is herewith set forth.

The carbides were extracted from the steels by three methods for electron microscopy and X-ray diffraction studies. The method which appeared to isolate the carbides in the least contaminated state was that developed by Mahla and Nielson. This employs a 10 pct solution of bromine in anhydrous methanol. The sample, as a solid piece, was allowed to stand fully immersed in the solution for a period of at least 24 hr. The spent solution then was carefully drained off and replaced by successive portions of fresh methanol until the wash liquid with the suspended particles remained water-white. The sample was agitated gently to free it of the residual particles and the residue was suspended in methanol and stored.

For electron microscopy the methanol was temporarily drained from the sediment of carbides and a portion of the sediment dispersed in distilled water. A drop of this suspension was placed on a polyvinyl formal coated specimen screen, allowed to settle, and the excess water drawn off with absorbent paper. When completely dry, the specimen was transferred to the electron microscope.

For X-ray diffraction, a portion of the sediment was allowed to dry and was transferred to a wedge-shaped holder in a circular camera. The Debye-Scherrer patterns were taken with unfiltered chromium K radiation.

The second extraction method involved electrolysis and was used chiefly to verify the results obtained with bromine-methanol. In this method the sample, with a surface area of about 3 sq cm, was made the anode in a beaker of 10 pct hydrochloric acid and current supplied at 6 v and 3 amp with a platinum rod cathode. In order to prevent attack on the extracted residue, a layer of glycerine about $\frac{1}{2}$ in. thick was first placed in the bottom of the beaker and the electrolyte poured in so that it floated on top of the glycerine. The isolated particles de-

a—5 min b—16 hr c—32 hr

Fig. 3—Typical chromium carbide types after heating at 1300 F. X10,000

tached themselves from the anode and dropped into the layer of glycerine, where they were protected from further chemical attack. When sufficient residue had collected, the electrolyte was siphoned off, and the glycerine layer containing the residual particles was treated several times with distilled water to remove the glycerine and finally was washed several times with ethyl alcohol. Then the particles either were allowed to dry or were stored in the alcohol.

The third extraction method was also electrolytic and was used to check the presence or absence of σ phase in the specimen. The sample was made the anode, and platinum the cathode in a solution composed of 300 g of copper potassium chloride ($2KCl \cdot CuCl_2 \cdot 2H_2O$), 100 ml hydrochloric acid (37 pct), and 900 ml of distilled water. A current density of about 2 amp per sq in. was used. The residue remaining after dissolving the sample was separated into two fractions in the following manner:

The electrolyte containing the residue was diluted to about twice its volume with ethyl alcohol. When this was done, many of the small particles which previously could be seen floating throughout the solution were made to concentrate at the alcohol-electrode interface and to rise to the top of the solution as the two liquids mixed. As it has been previously found that any σ phase in stainless steel extractions is concentrated in the floating scum, the scum was removed from the surface of the liquid with a glass slide and allowed to dry thoroughly on the slide with subsequent washing in distilled water to dissolve the chemical salts. The material remaining on the slide after a final drying was transferred to the specimen holder and placed in the X-ray camera. Incidentally, no σ phase was found in any of the specimens.

The samples were prepared for metallographic examination and electron microscopy by specially developed techniques. The surface to be studied was ground in the usual manner on abrasive papers and polished on hard cotton cloth carrying calcine-prepared γ-type alumina. Since the surface left on a metal specimen even after a most careful mechanical polish is not in a completely undistorted state, the polishing was finished electrolytically. Here the specimen was made the anode in a solution consisting of 10 parts of perchloric acid (70 pct) and 90 parts of glacial acetic acid. The cathode was a large sheet of stainless steel. A potential of 110 v dc at a current density of 3 to 6 amp per sq cm was applied for four 15-sec intervals.

The samples were etched by immersion in a 25 pct solution of hydrochloric acid in ethyl alcohol for 10 to 30 min, depending upon the heat treatment they received (i.e., their relative corrodibility). The optical micrographs were taken, and subsequently replicas were taken, from the same surfaces for electron microscopy.

The replica method employed was a modification

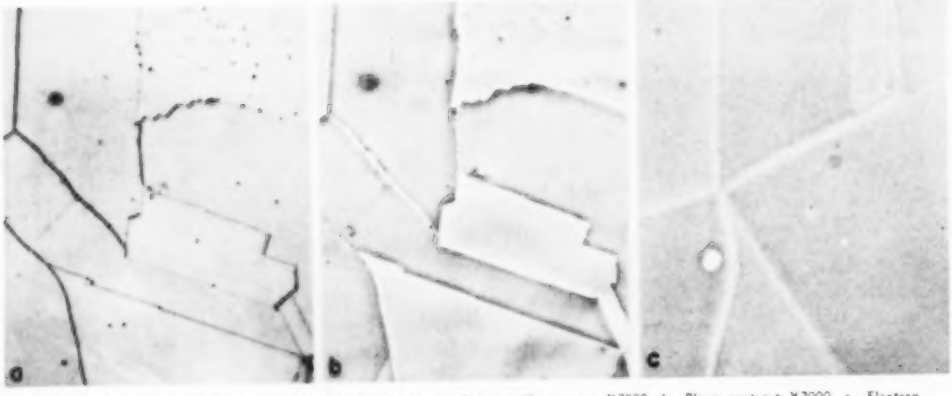


Fig. 4—Surface contour of sample heated 100 hr at 1200 F. a—Ordinary illumination, X2000. b—Phase contrast, X2000. c—Electron microscope, X10,000. HCl etch.

of existing techniques. The surface to be examined was first cleaned by flooding with a 2 pct solution of polyvinyl formal in ethylene dichloride, finally leaving on the surface a thick, strong film which was easily removed by dry stripping with transparent adhesive tape. This film was discarded and the surface of the specimen was flooded with a more dilute solution of polyvinyl formal (0.5 to 0.75 pct) and the sample drained at an angle of about 90° to the vertical. When thoroughly dry, a 35 pct aqueous solution of polyvinyl alcohol was applied in suitable thickness to the coated surface as a reinforcing backing. After a period of from 2 to 16 hr, depending upon the thickness, the aqueous polyvinyl alcohol reached a consistency whereby it, together with the underlying fragile film, could be readily stripped from the metal surface. When the backing was quite thin, transparent adhesive tape was used as the means of stripping. The reinforced replica was then placed in distilled water to dissolve the backing strip, thus freeing the replica and separating it from the tape when the latter was employed. The replica was removed, subjected to a series of washings in fresh distilled water, cut to suitable size, and placed on the specimen screens.

The results of the extractions were illuminating. X-ray diffractions showed only the Cr_3C_2 type structure. In Figs. 1, 2, and 3 the carbide extractions are shown at 10,000 and 20,000 diameters. These were enlarged from electron micrographs obtained at 6000 diameters. One of the first observations to be made, and one which should be borne in mind in all of the following, is that in practically all cases the carbides were essentially flat, i.e., two-dimensional in character rather than three-dimensional. The exceptions are rods and the small cubes noted in Fig. 2d. This two-dimensional characteristic is consistent with other observations to the effect that chromium carbide precipitation takes place largely at grain and lattice interfaces. The leafy type shown in Fig. 1 (Ia, Ib, and Ic) and Fig. 2a is one of the earliest forms to appear with respect to time and temperature of precipitation, and the rectangular grid type shown in Fig. 1 (IIa, IIb, and IIc) and Fig. 2b is another early type with respect to time and temperature. The triangular type is shown in Fig. 1 (IIIa, IIIb, and IIIc) and Fig. 2c. The cubes shown in Fig. 1 (IVa, IVb, and IVc) and Fig. 2d occurred in

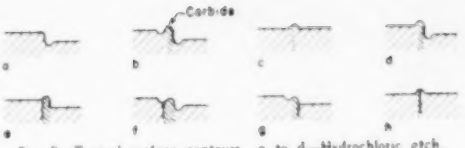


Fig. 5—Typical surface contours. a to d—Hydrochloric etch. e to h—Hydrochloric etch plus nitric treatment.

minor amounts at all precipitation temperatures. At temperatures at and above 1300°F, the plates, ribbons, and rods shown in Fig. 1 (Va, Vb, and Vc) and Fig. 2c appeared and were present to a still greater degree as the temperatures were increased. With time and temperature each of these types tends to grow, as shown.

With respect to time at 1300°F, only the leafy form appeared in the 5-min specimen; the other forms made their appearance as the time was increased up to 32 hr. These are shown in Fig. 3 where it will be noted that early forms of the leaf, grid, triangular, and ribbon and rod types are all present. Heating for more than 32 hr resulted in coarsening but no other changes in character.

Before attempting to put the pieces together as it were, let us consider the locale of precipitation as evidenced by the micrographs. The hydrochloric acid etch attacks different grains at different rates, thus providing contours at different levels. This is shown clearly in Fig. 4, which compares the appearance of a specimen under the optical microscope with and without phase contrast and under the electron microscope. Local zones of greater attack are also evident at grain and twin interfaces. The carbides are attacked less rapidly than the metal matrix and stand in relief. As shown in Fig. 6, a similar local attack occurred at interfaces in the annealed specimen, as might be expected from the lattice distortion existent at such boundaries even though no carbide was present. If we were to cut a plane normal to the interface, the contour intercepted on that plane would be as shown in Fig. 5a. Micrographs are shown after the precipitation treatment at 1000° to 1500°F at 100° intervals in Figs. 7 to 12, as well as for the samples subjected to precipitation at 1300°F for 5 min, 2, 8, and 32 hr in Figs. 13 to 16. Typical grain boundary contours of these specimens are sketched in Figs. 5b, c, and d.

Fig. 6—Annealed sample. a—Optical, X2000. b—Electron, X10,000. HCl etch.

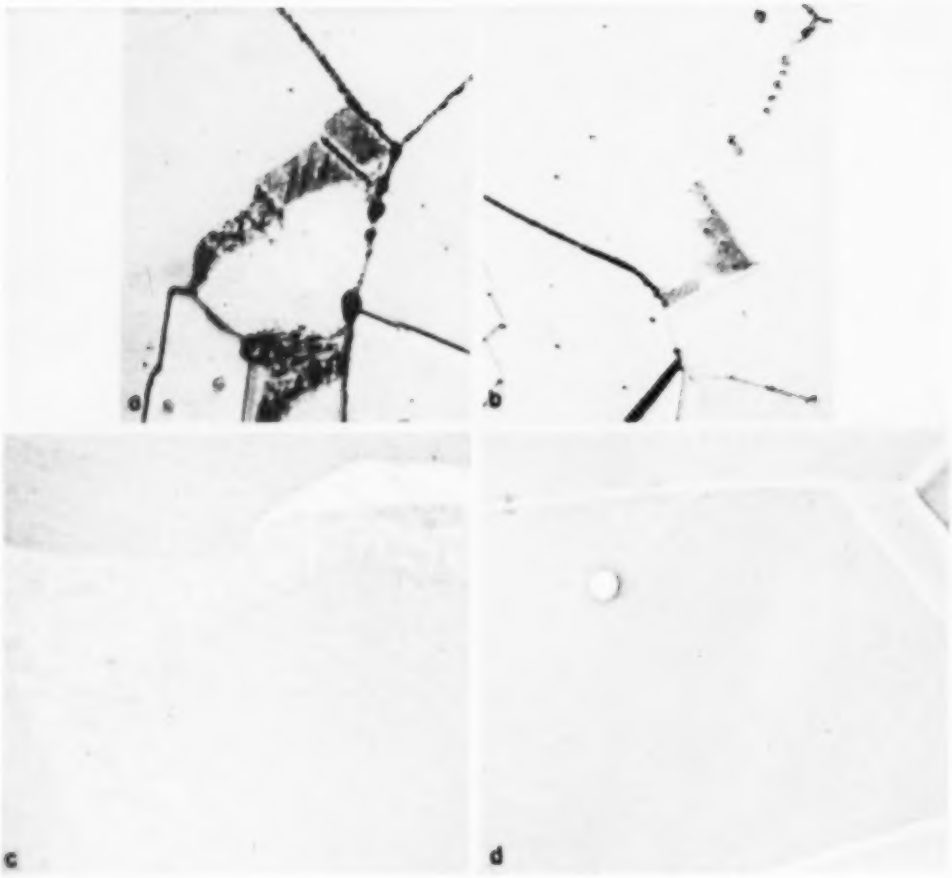


Fig. 7—Sample heated 100 hr at 1000 F. a, b—Optical, X2000. c, d—Electron, X10,000. HCl etch.

Fig. 8—Sample heated 100 hr at 1100 F. a—Optical, X2000. b—Electron, X10,000. HCl etch.

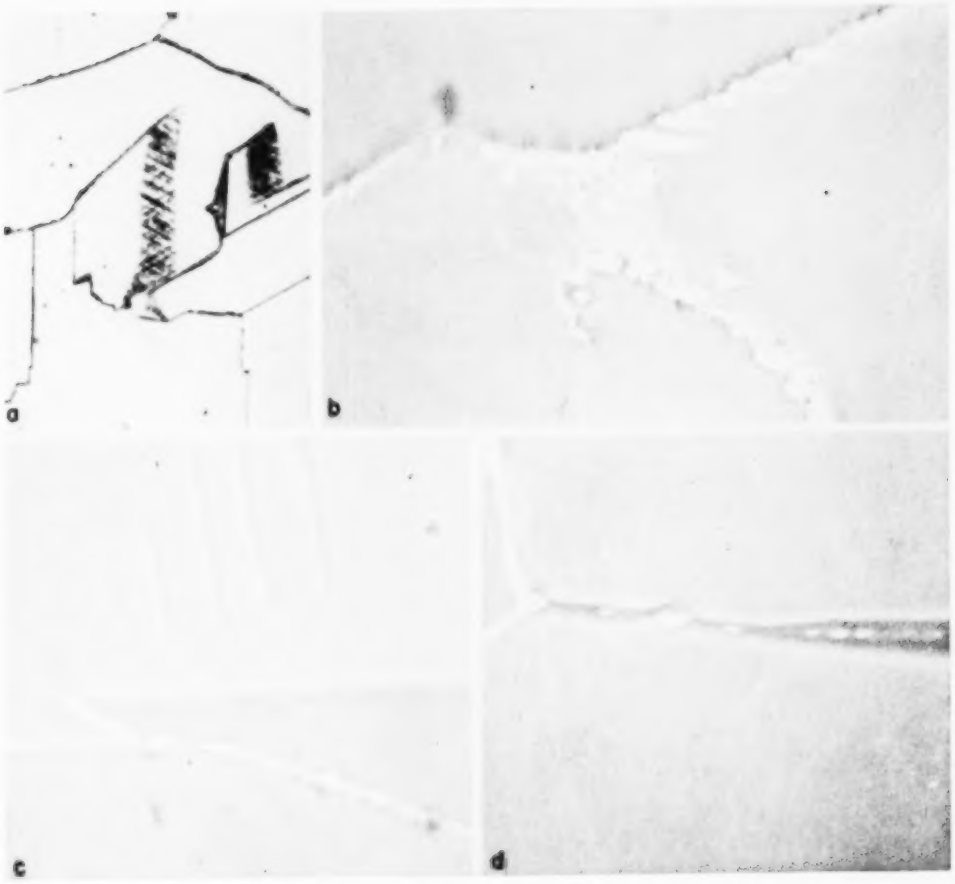


Fig. 9—Sample heated 100 hr at 1200°F. a—Optical, X2000. b to d—Electron, X10,000. HCl etch.

A brief description of significant features would seem to be in order. In the annealed state there is a total absence of carbides. After 1000°F precipitation treatment, the carbides are present at grain boundaries with a very few possibly present at the ends of twins but not at the twin sides. After 1100°F, the situation is not materially different, but the carbides are more clearly developed and there is some evidence of carbide precipitation at twin sides. After 1200°F, the attack on all interfaces is severe with good definition of the carbides and an obvious increase in particle size. Further, carbides are evident on twin sides and etch lines are apparent within the grains. These may or may not be related to carbide precipitation. After 1300°F, carbides are much coarser, there are more of them and additional carbides have grown on planes at right angles to the original carbides and into the grain. After 1400°F, carbides are quite coarse and large growths occur particularly at the twin ends. Carbides have also precipitated within the grains. The structure shown in Fig. 11 is of particular interest. After 1500°F, the carbides are still more massive and the precipitation is fairly general within the grains, but the essential character is not different.

Even a glance at the photographs shows a relation between the extracted carbides and the carbides remaining in the electron micrographs. Careful study and comparison of the extracted carbides with their shape, location, and occurrence in the structures illustrated by the optical and electron micrographs show a very definite correlation. While the following observations may not be taken to establish a universal truth, they are sufficiently striking as to form an inference with a major probability of universality. The leaves form at 1000°F at grain boundaries and with increasing precipitation temperature they grow and finally change to a more massive dendroidal form. The grids, fine and of a two-dimensional form at 1000°F, are well developed with particles of substantial thickness at 1300°F and continue to grow and provide increasingly well-defined crystals at higher temperatures. Most significantly, however, the qualitative relationship be-

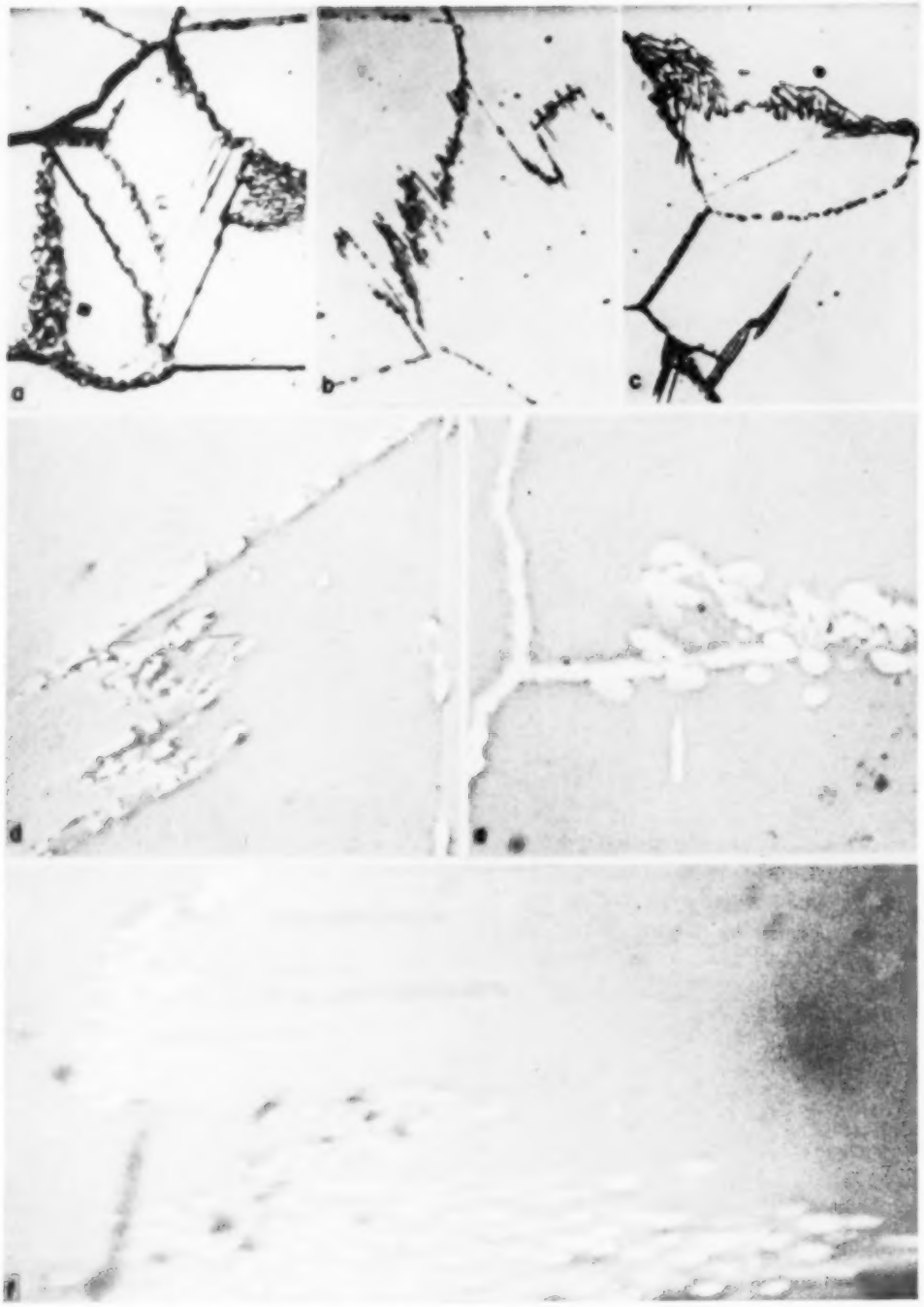


Fig. 10—Sample heated 100 hr at 1300° F. a to c—Optical, X2000. d to f—Electron, X10,000. HCl etch.

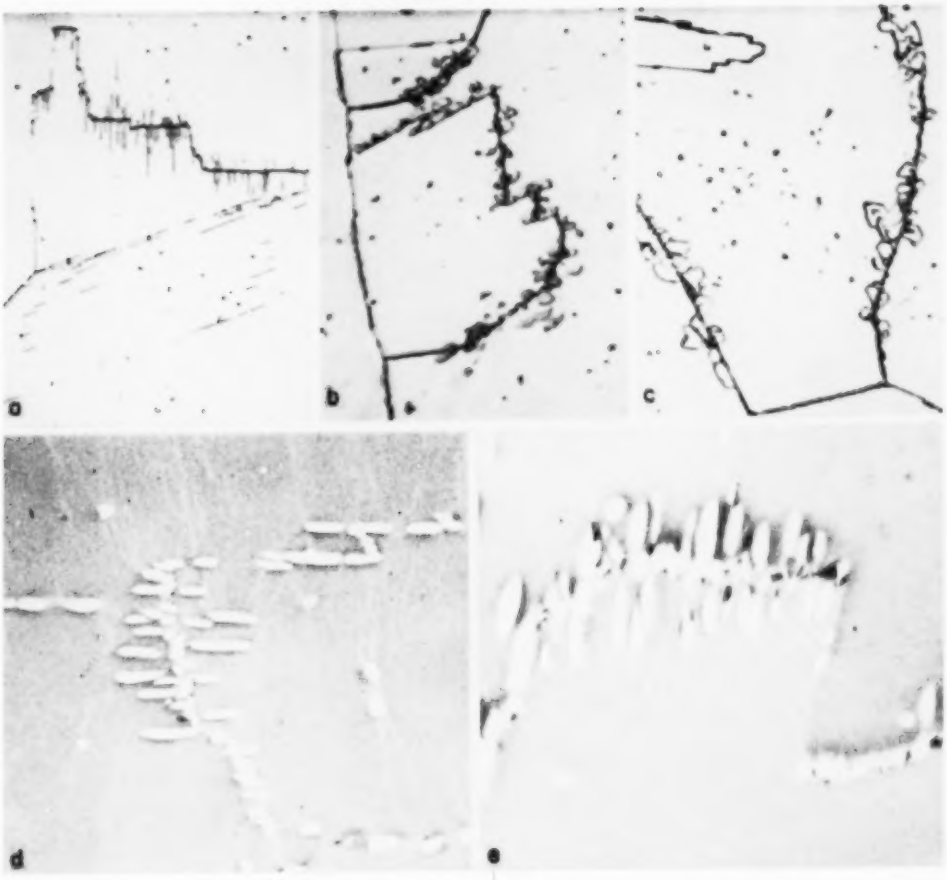


Fig. 11—Sample heated 100 hr at 1400 F. a to c—Optical, X2000. d to e—Electron, X10,000. HCl etch.

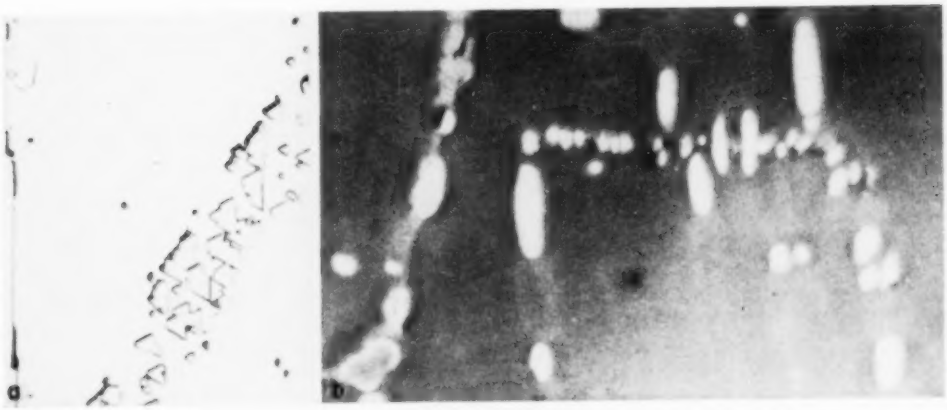


Fig. 12—Sample heated 100 hr at 1500 F. a—Optical, X2000. b—Electron, X10,000. HCl etch.

Fig. 13—Sample heated 5 min at 1300 F. a—Optical, X2000. b—Electron, X10,000. HCl etch.

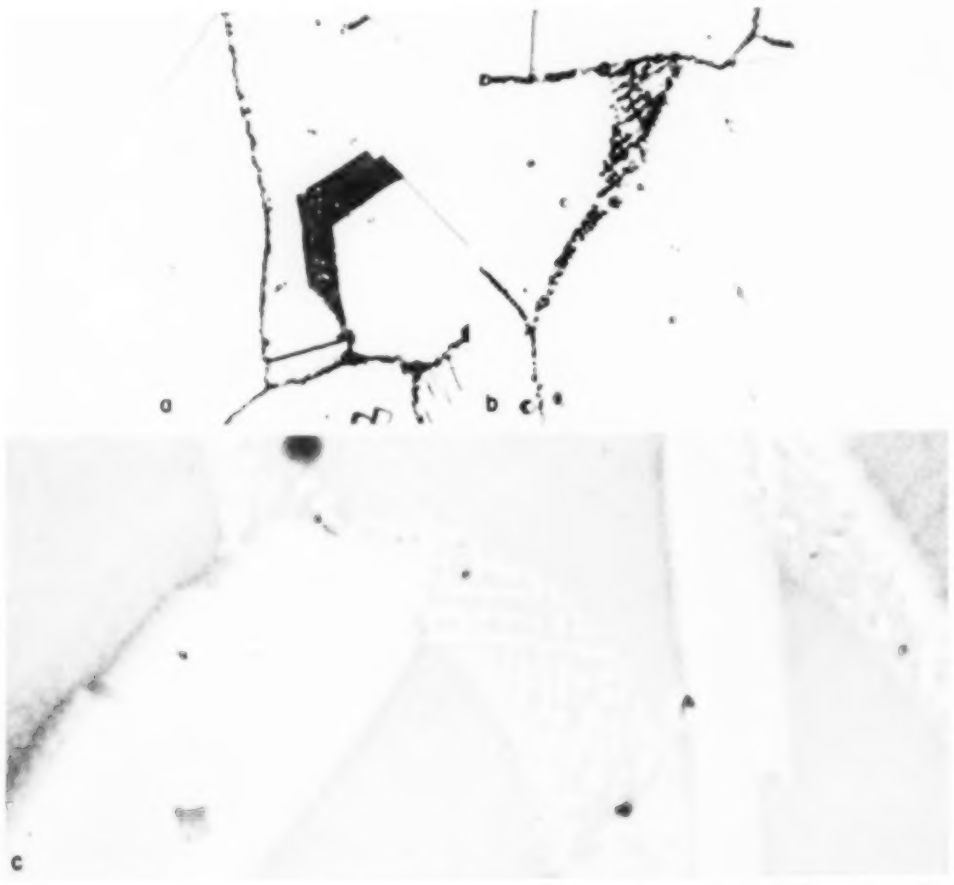


Fig. 14—Sample heated 2 hr at 1300 F. a, b—Optical, X2000. c—Electron, X10,000. HCl etch.

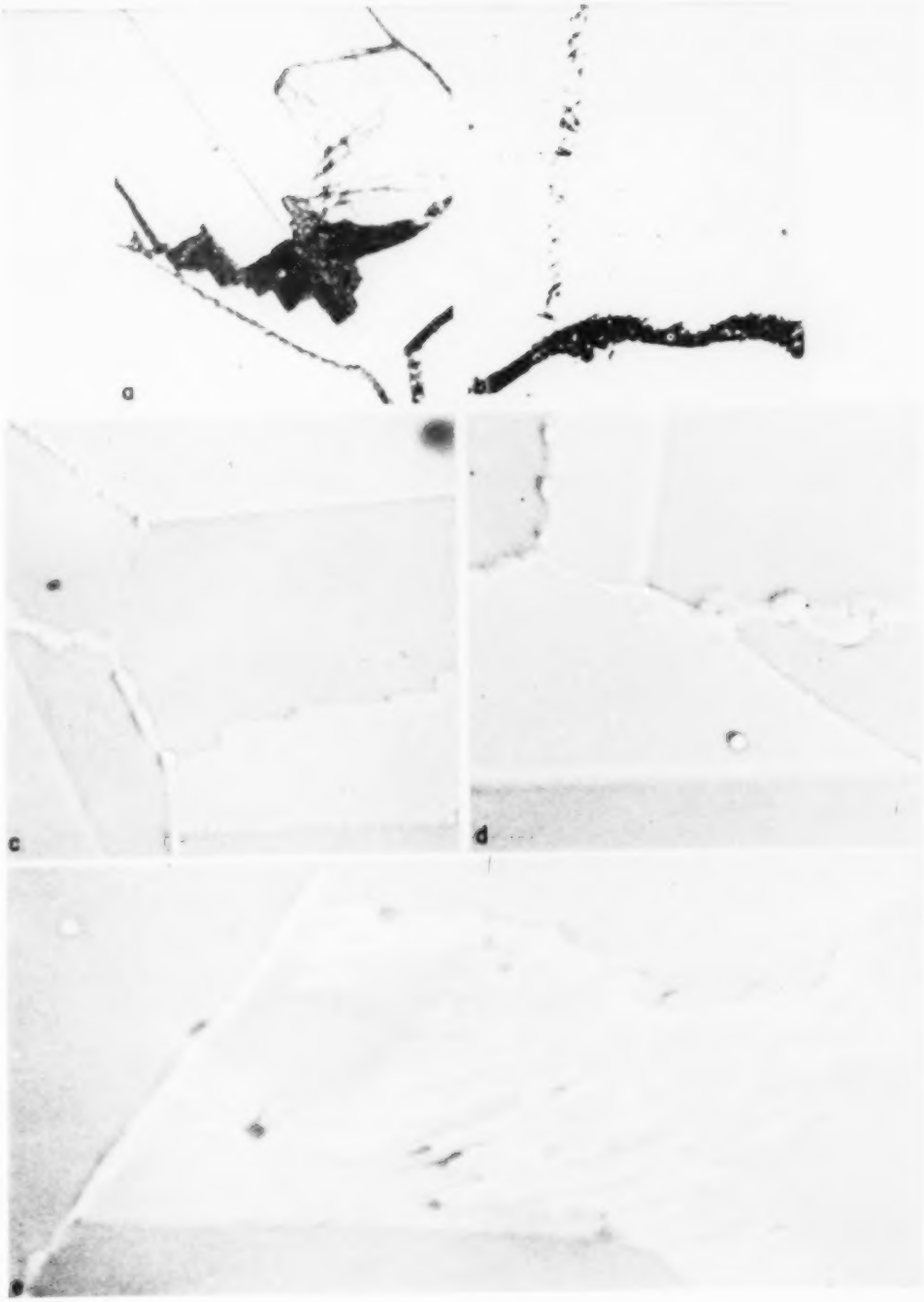


Fig. 15—Sample heated 8 hr at 1300 F. a, b—Optical, X2000. c to e—Electron, X10,000. HCl etch.

Fig. 16—Sample heated 32 hr at 1300 F. a—Optical, X2000. b—Electron, X10,000. HCl etch.

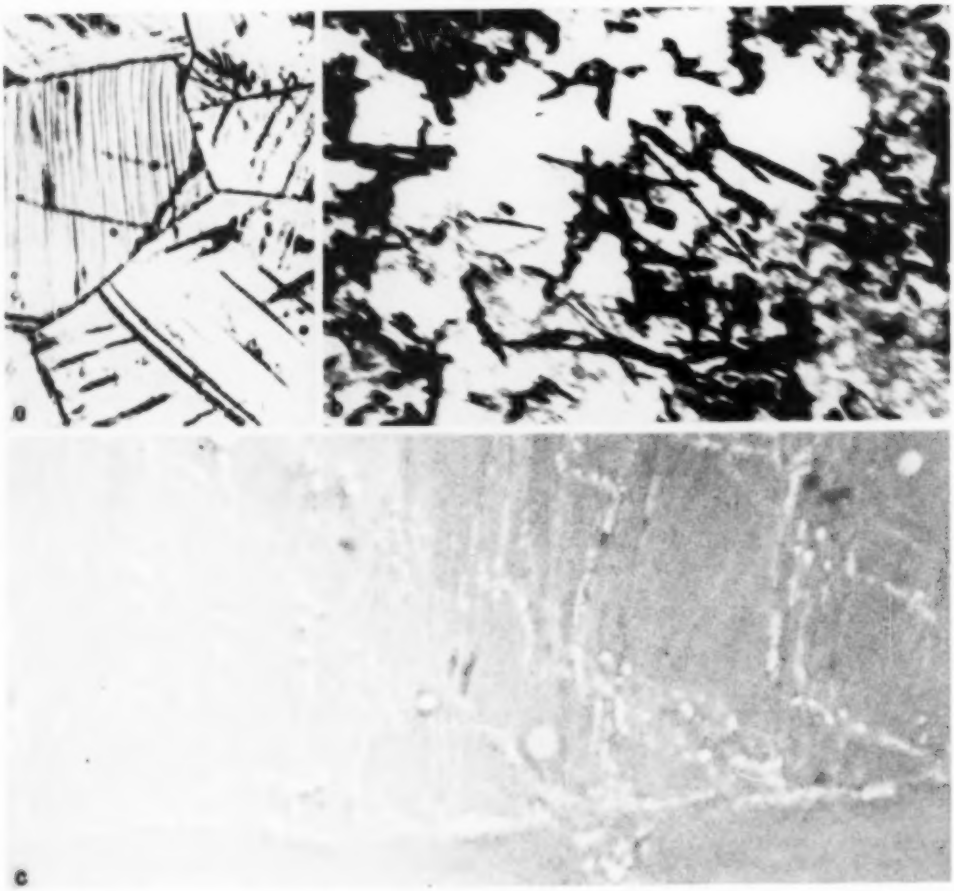


Fig. 17—Cold rolled sample heated 1 hr at 1200 F. a—Optical, X2000. b—Chromium carbide, X20,000. c—Electron, X10,000. HCl etch.

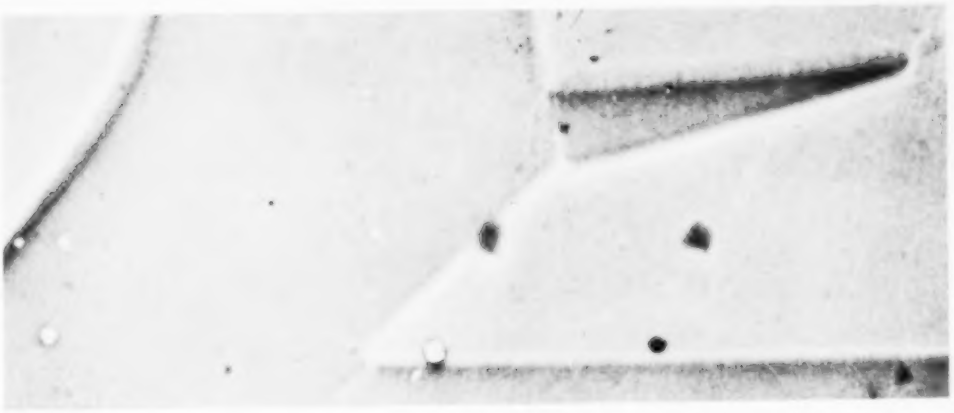


Fig. 18—Annealed sample. HCl etch plus HNO_3 treatment. Electron. X10,000

tween the extracted carbide grids and the micrographs shows that the grids occur at twin ends. The triangular types, virtually absent after 1000 F treatment, are present in abundance at 1200 F and in even greater number and size at higher temperatures as ordered ranks of continuously connected particles. Again correlation of the extractions and micrographs gives strong evidence that the triangular types occur initially at the sides of twins. The plates, ribbons, and rods occur at precipitation temperatures above 1300 F, and again study of the evidence shows that they, together with latterly developed triangles, correspond to carbide formations on lattice planes. These carbides grow from initially precipitated carbides and also grow generally within the matrix. The cubes occur at all precipitation temperatures, but the number is so small and the occurrence so rare that they would seem to have no significance.

All of the foregoing correlation applies to observations on samples subjected to precipitation treatment for 100 hr. Similarly, after a precipitation treatment of 5 min at 1300 F, only leaves are present at grain boundaries and only at a few. After a 2 hr precipitation treatment, the leaves are more numerous and in addition grids are present at twin ends. After an 8 hr precipitation treatment, the leaves and grids are coarser and in addition triangles are present at twin sides. After a 32 hr precipitation treatment, all of the above forms are present with carbides somewhat coarser throughout, but in addition the triangular particles are much more clearly defined.

What, then, is the meaning of these observations? Perhaps it may be summed up broadly by the concept of registry offered by Mehl and Jetter. In the chromium carbide precipitation the atom lattice of the precipitate matches with some degree of registry the atom lattice of the matrix surface. This, of course, would produce a distortion at the interface and would also produce crystallographic forms related to the nature of the interface. It is somewhat difficult to trace the specific geometry of a lattice on a twin boundary which results in a flat triangle, but it is not very difficult to imagine. Similarly, it is not surprising to find hexagonal ribbons and plates or flat triangles on planes within a grain and the less well-defined geometrical shapes such as leaves at the grain boundaries. Moreover, the degree of regularity expected at the end of twins can explain the grids.

Let us approach in a somewhat different way. In a simple cubic crystal of high symmetry such as Cr_3C_2, there are crystallographic planes of unusually dense atomic packing. These planes have very low surface energy when exposed at a crystal face. A growing crystal tends to approach a condition of minimum surface energy by reducing surface area or by terminating as a crystal with only low energy planes as faces. The lowest energy forms in the case of chromium carbide are probably the cubic (100) planes and the octahedral (111) planes. Either of these forms might predominate, depending upon the planes of the austenitic matrix along which the carbide is growing. In the case of the triangular flat plates, it is very likely that (111) planes in the austenitic matrix (which have a trigonal or hexagonal symmetry) have exerted a controlling influence on the external shape of the precipitate.

From the foregoing, always remembering that these carbides are essentially two-dimensional in character, we conclude that the perfection of geometric form of the carbide is a direct function of the degree of registry of the lattice planes on either side of the interface in which the carbide is precipitated.

If the foregoing is tenable, we should expect that the nature of precipitation will be radically altered by cold-working. To check this, an annealed specimen $\frac{1}{2}$ in. thick was reduced 25 pct in thickness by cold-working, thus providing thin and irregular cells between slip planes differing only slightly in orientation. Examination after cold-working showed etching on strain lines and absence of carbide. The sample was then subjected to precipitation treatment of 1 hr at 1200 F. Examination of the microstructure showed (Fig. 17) carbide precipitation at grain boundaries with similar and relatively voluminous precipitation throughout the grains along the slip planes. These carbides were in the form of elongated leaves, irregular rather than geometric in shape, all of which is consistent with the concept of registry.

The relation of the precipitated carbide to localized interface attack from nitric acid or copper sul-

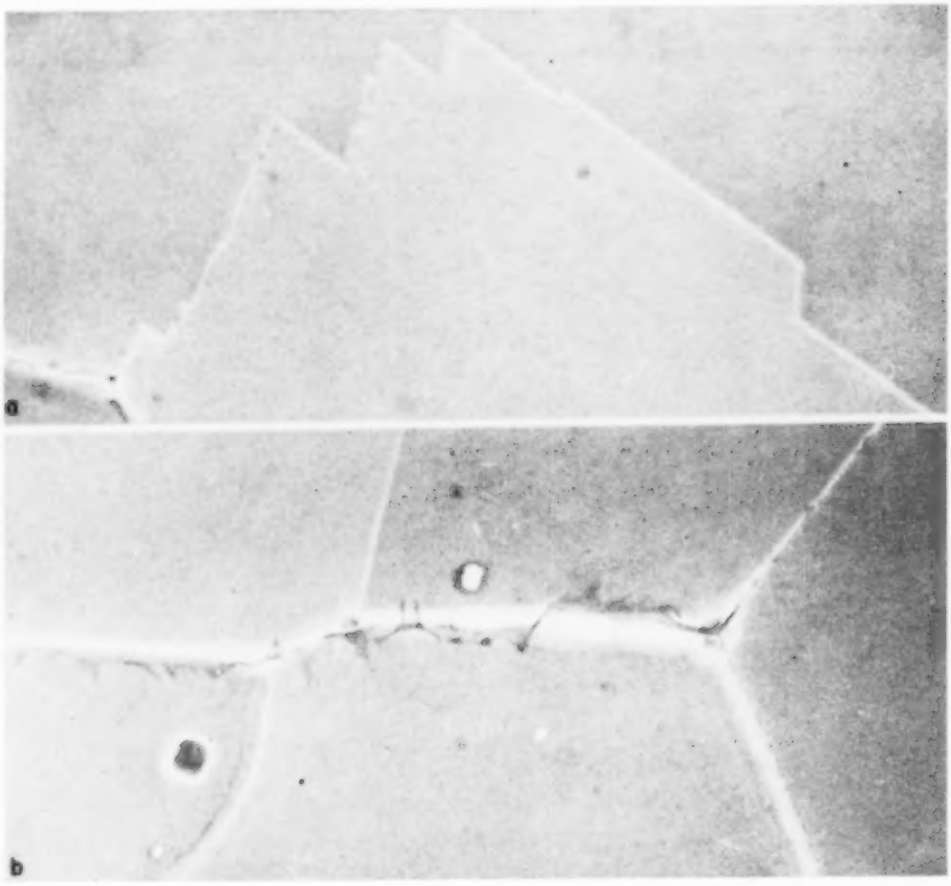


Fig. 19—Sample heated 100 hr at 1000 F. Electron, X10,000. HCl etch plus HNO_3 treatment

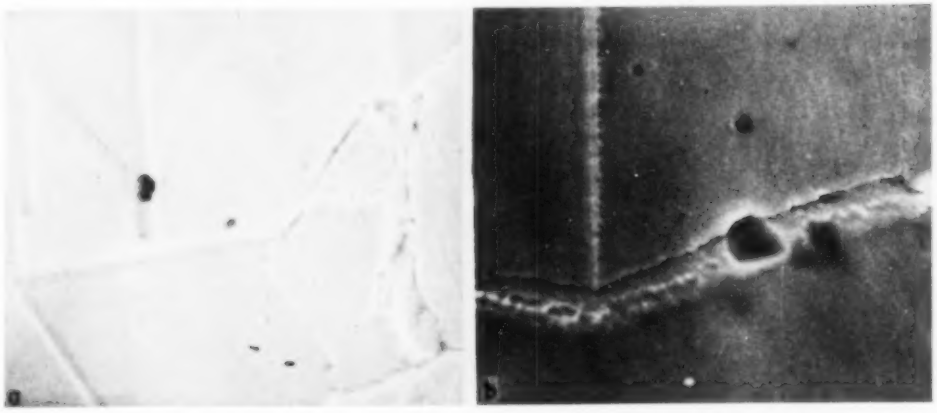


Fig. 20—Sample heated 100 hr at 1100 F. Electron, X10,000. HCl etch plus HNO_3 treatment

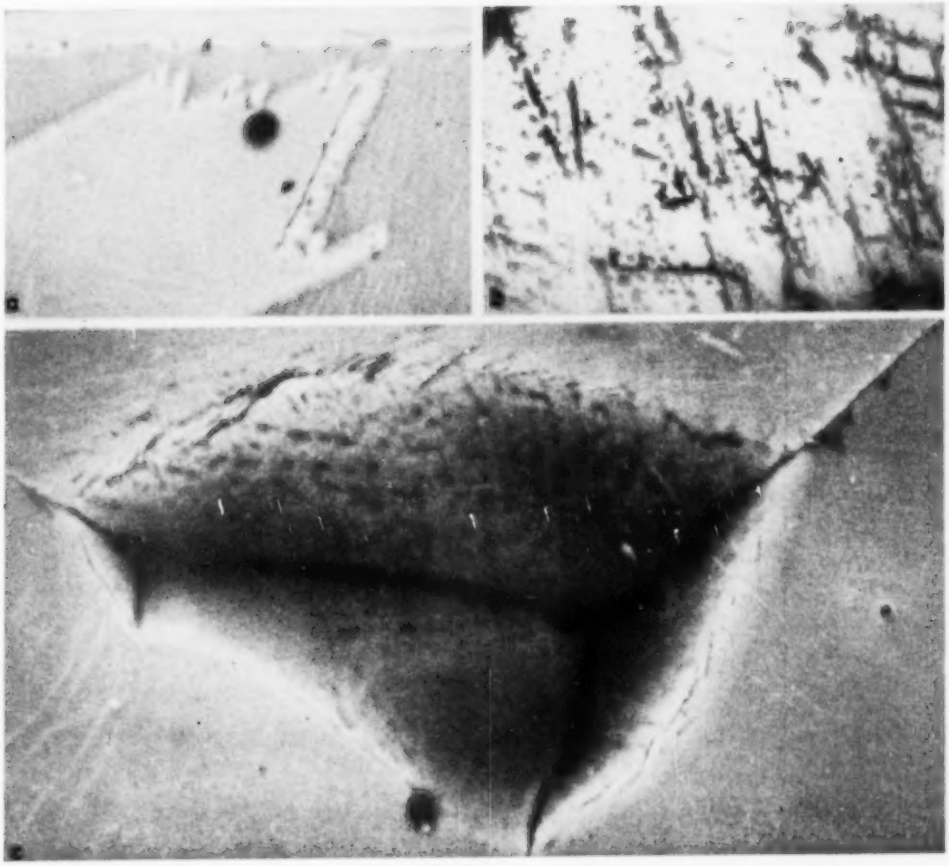


Fig. 21—Sample heated 100 hr at 1200 F. Electron, X10,000. a—HCl etch plus HNO_3 treatment. b, c—Copper sulphate treatment.

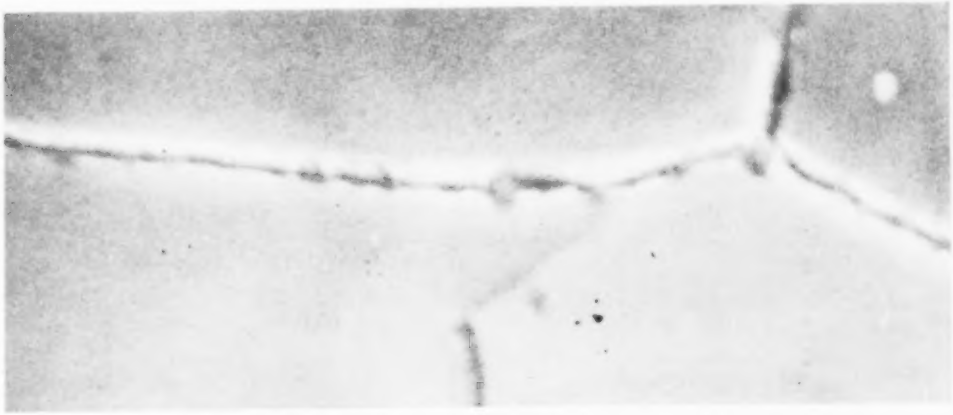


Fig. 22—Sample heated 100 hr at 1300 F. Electron, X10,000. HCl etch plus HNO_3 treatment.

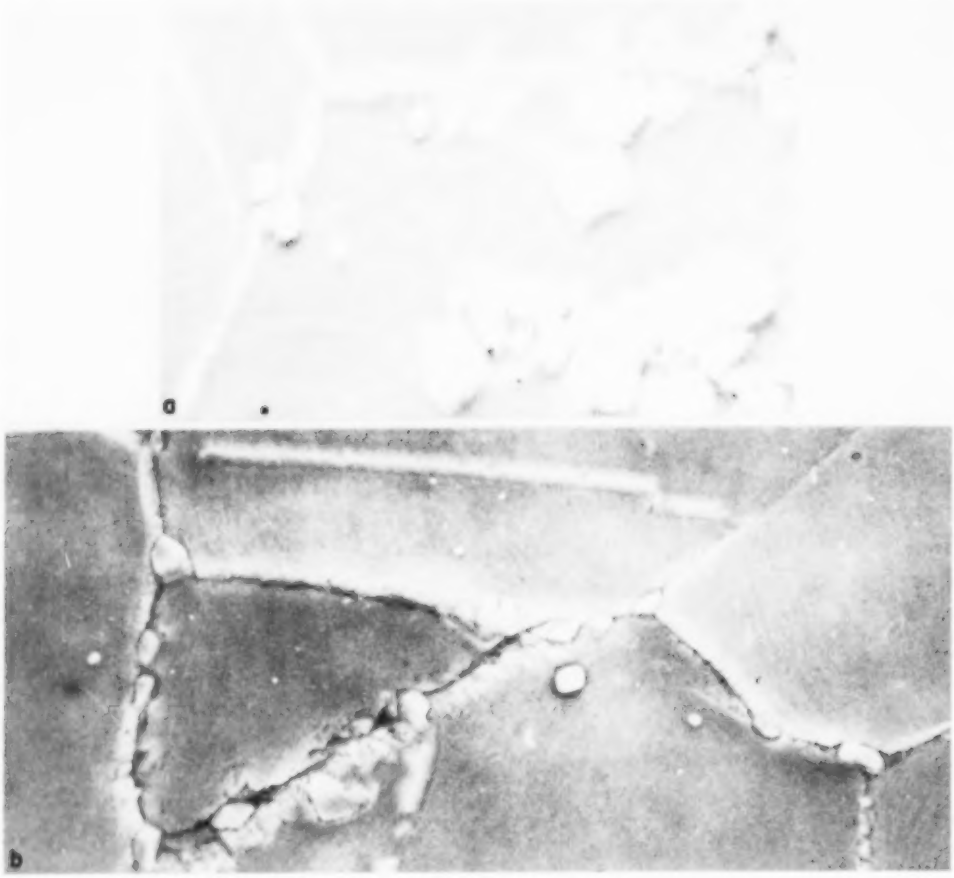


Fig. 23. Sample heated 100 hr at 1400 F. Electron. X10,000. HCl etch plus HNO_3 treatment.

phate-sulphuric acid solution is of particular interest. Accordingly the specimens so etched corrosion-wise were examined in the microscope and replicas examined in the electron microscope. Electron micrographs of specimens first etched in hydrochloric acid to bring carbides into relief and subsequently etched in nitric acid or copper sulphate solution are shown in Figs. 18 to 28 for the annealed sample, as well as the 100° interval precipitation treatments and the short time treatments at 1300° F.

As was to be expected from the vast amount of work previously done in this field there was no localized attack in the annealed specimen, although the grain edges were slightly more attacked than the matrix proper. After a 1000° F precipitation treatment, there was localized interface attack both at grain boundaries and at twin ends. The contours corresponding to these are shown in Figs. 5e, f, g, and h. The knife-edge attack in Figs. 19a and b is striking. Fig. 19b deserves special mentaon in that here it would seem the replica had penetrated the knife-edge opening and after removal from the specimen had been folded over. This micrograph is further noteworthy in that it shows knife-edge attack at one edge of the carbide and then at the other edge of the carbide at the same grain boundary. The entire series of micrographs shows that the knife-edge attack never occurs on both sides of the carbide at any point. After an 1100° F precipitation treatment, knife-edge attack occurs at twin sides as well as at grain boundaries and twin ends. After 1200° F, the highly localized attack is quite severe. In many instances, such as in Fig. 21b, the grains were lifted out and the interface carbides remained attached to the remaining surface. It is particularly significant that in no case, and this may be well seen in Fig. 21b, was there any evidence of gross attack on the metal immediately adjacent to the carbide particles. After 1300° F, the specimens were not essentially different than after 1200° F, although the localized attack occurred at nearly all interfaces. The attack after a 1400° F precipitation is particularly interesting in that it is in general less severe and much longer corrosion time is necessary for knife-edge attack at the grain boundaries. Moreover a general gouging rather than knife-edge attack takes place on twin ends and sides, as well as those grain boundaries which may or may not show knife-edge attack. This may best be visualized by contour sketches Figs. 5f and g. After a 1500° F

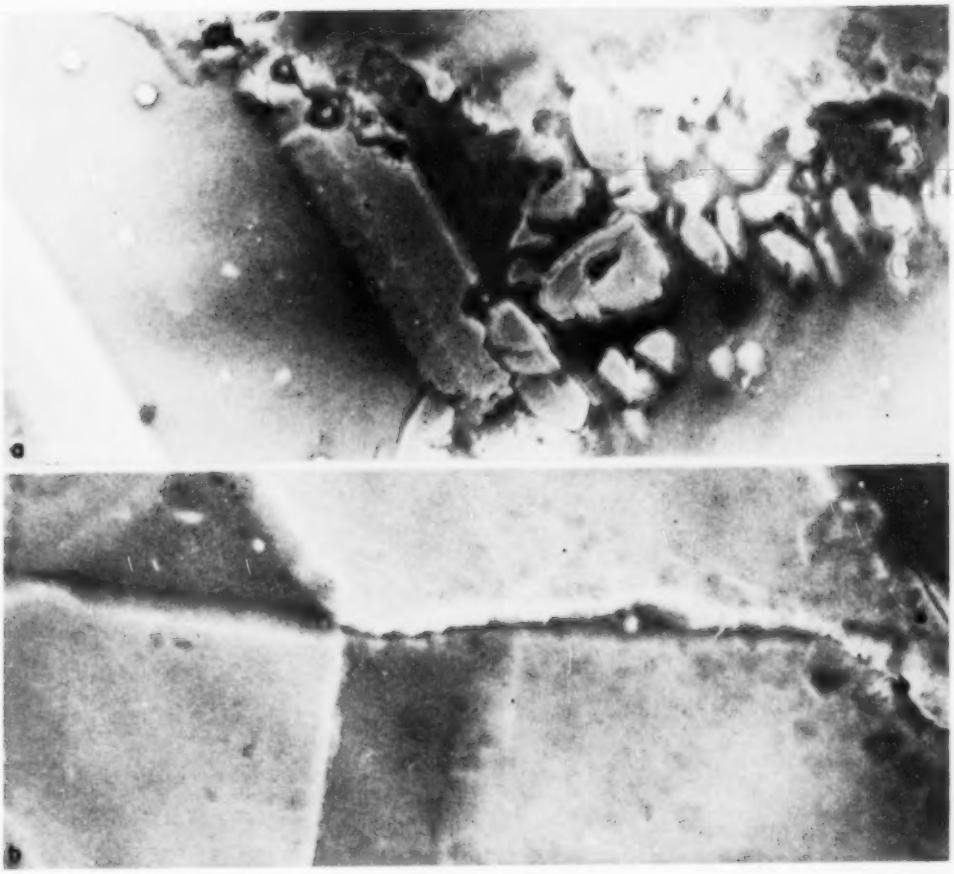


Fig. 24—Sample heated 100 hr at 1500 F. Electron, X10,000. HCl etch plus HNO$_3$ treatment.

treatment there was no local boundary attack of knife-edge character in the boiling nitric acid. The general attack in the area was around the carbide and similar to that on the sample treated at 1400 F. It should be noted that the black line in Fig. 24, which might be construed to show knife-edge attack when viewed directly in the microscope proper, is clearly no more than an edge effect from gouging. At no time during the corrosive attack was there interface separation typical of the knife-edge corrosion found in the specimen treated at 1300 F. Thus it is evident that the nature of the chemical attack is qualitatively quite different than that which occurs after precipitation treatment at 1300 F, where true interface separation occurs as evidenced by the knife-edge contour.

How does all of this correlate with the aforementioned observations and hypothesis? Obviously there is a potential difference between the carbide and the matrix, and the knife-edge attack would appear to be electrolytic in character. Accordingly attempts were made to measure the potential of synthetically produced massive chromium carbide (Cr_3C_2). This proved to be more than difficult in that this chromium carbide behaved similarly to stainless steel with changing potential as passivity was or was not a controllable factor. However, enough measurements were made so that it could be concluded that the chromium carbide was more noble than the stainless steel. Separate experiments have shown that the potential of the extracted carbides was well represented by that of the synthetic carbide. Further, a specimen of carbide attached to a piece of annealed 18-8 with the whole immersed in nitric acid showed attack of the 18-8, the general attack being accentuated at the grain boundaries. A similar experiment, wrapping a piece of platinum wire around the 18-8, gave the same results. From all of this we may conclude that precipitated chromium carbides in an austenitic stainless steel matrix do set up a potential at interfaces and that this potential is of such order as to be a major factor in the nature of the corrosion.

What causes grain boundary attack to be a local knife-edge penetration in one case and a more general gouging in the other? Both forms of attack result from electrochemical reaction between carbide and matrix in oxidizing acid media. The knife-edge attack requires a corroding reagent that is strongly oxidizing in character, which suggests that

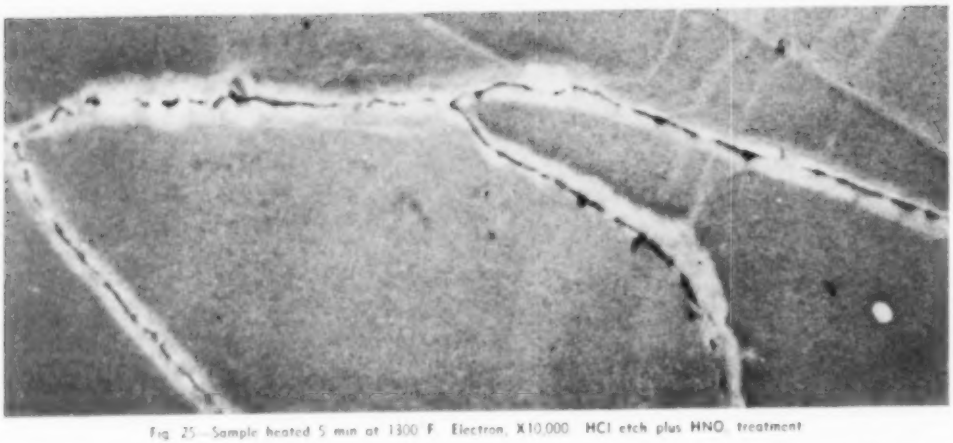


Fig. 25—Sample heated 5 min at 1300 F. Electron, X10,000. HCl etch plus HNO_3 treatment.

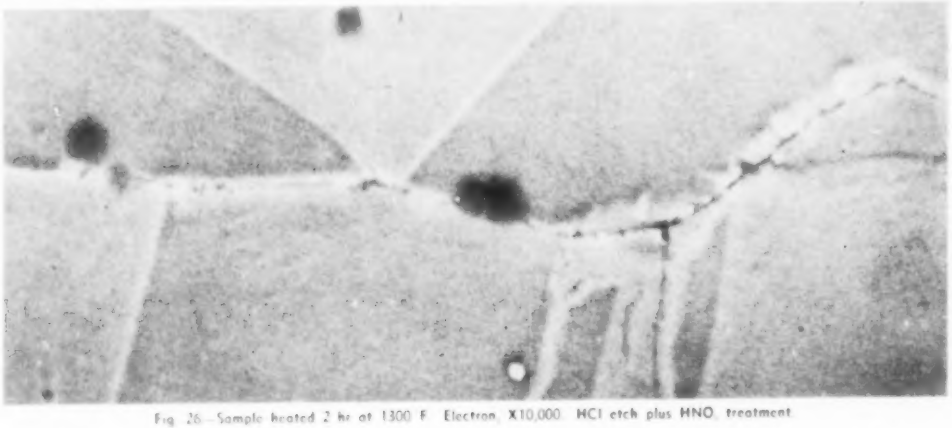


Fig. 26—Sample heated 2 hr at 1300 F. Electron, X10,000. HCl etch plus HNO_3 treatment.

one member of the couple must be ennobled by passivation in order to make it strongly cathodic. While the more general type of attack may proceed under less oxidizing conditions, such changes alone in the environment do not explain the qualitatively different forms of attack resulting from carbide precipitation. It would, therefore, appear that the character of the interface subject to local knife-edge attack is qualitatively different from that not subject to such attack.

In dealing with an interface in which a carbide has formed, we must consider that the initial formation takes place in one or the other of the lattices forming that interface. If the degree of registry of the two matrix lattices is small, then the carbide will continue to grow, following the planes and positions of the lattice to which it is registered and, in its fully grown form, the atomic structure of the carbide proper will be essentially out of registry with the other lattice of the original interface.

Thus it is evident that after precipitation of carbide in an interface of low registry, one of the carbide-matrix boundary zones will have a relatively high energy level. This is consistent with the observation that knife-edge attack occurs only on one side of the essentially two-dimensional carbide precipitate. Further, the degree of severity of knife-edge attack is greatest at grain boundaries and progressively less severe at twin ends and twin sides, until finally no attack is observed on carbides precipitated on lattice planes within the matrix proper. From this it is concluded that the energy level of the carbide-matrix boundary zone is proportional to the lack of registry of the carbide-matrix interface and, in turn, to the lack of registry of the original matrix interfaces. Secondary growth of carbide at higher temperatures into the matrix from the surfaces of the original carbide on lattice planes effectively eliminates interfaces of gross lack of registry between carbide and matrix. Thus, it is concluded that the local knife-edge attack results from and is proportional to lack of registry of the initial matrix interface.

Hypotheses to account for the effect of matrix registry on knife-edge attack are interesting, but speculative. These hypotheses may be reasoned from the viewpoint of chemical inhomogeneity, mechanical strain, their combined effects, or more abstruse mechanisms. Chromium depletion has long been discussed as a cause of a localized interface attack, but convincing evidence has not been developed either to refute it or to substantiate it. With

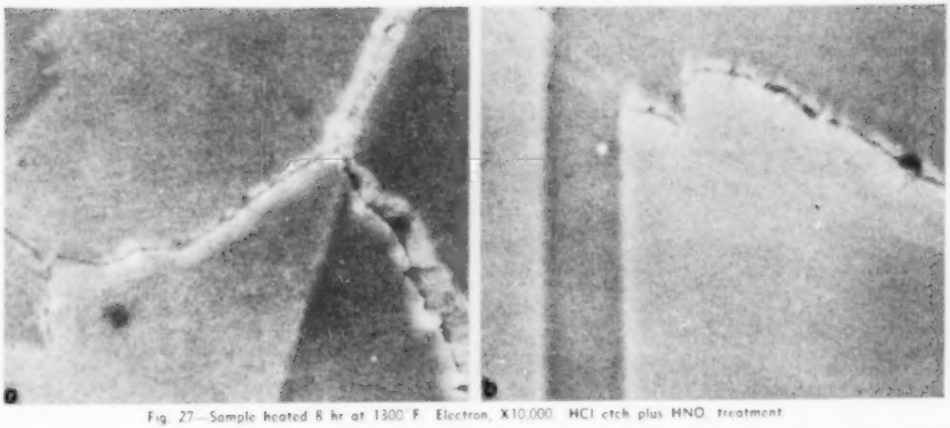


Fig. 27—Sample heated 8 hr at 1300 F. Electron, X10,000. HCl etch plus HNO_3 treatment.

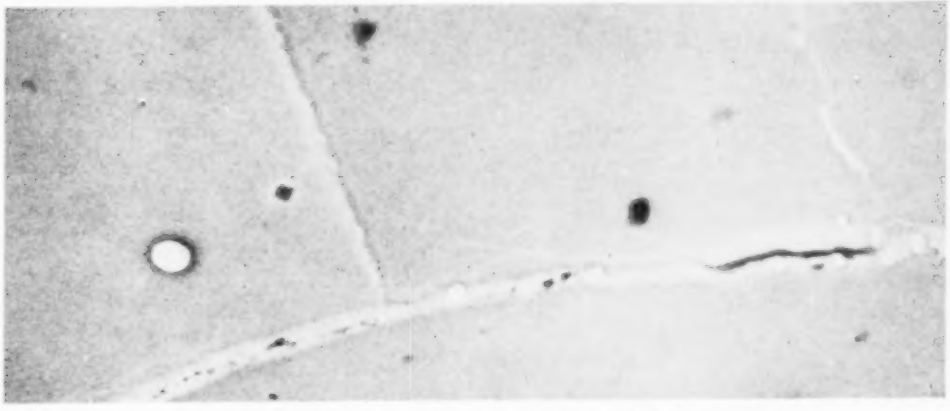


Fig. 28—Sample heated 32 hr at 1300 F. Electron, X10,000. HCl etch plus HNO_3 treatment.

respect to registry it might be presumed that diffusion proceeds more rapidly along certain lattice planes, so that the concentration gradient normal to an interface would be more pronounced on one side and that the carbide would tend to grow faster on one side. Opposed to this is the fact that precipitation in an interface of a high degree registry does not result in knife-edge attack, even though a significant concentration gradient may exist. In a similar manner an equally good, but still unsubstantiated, case may be made for mechanical strain.

There is a very high order of mechanical cohesion between the precipitate and each adjoining lattice. This is readily understood with respect to the lattice to which the carbide is registered, but there is an implication that within the second lattice the atoms near the interface either have an extremely low order of mechanical cohesion, which is not the case, or that they are arranged in a pattern strongly influenced by that of the carbide, which therefore must be the case. This means that there is a high degree of strain at that interface. In other words lack of registry results in strain. The order of the degree of strain is therefore related to the lack of registry existing before a carbide was formed. At twin sides this is so small as to produce only a slight strain effect. At twin ends it is greater and at grain boundaries it would generally be maximum. This is entirely consistent with observations on knife-edge attack, as maximum corroding conditions are necessary to produce this attack at twin sides, severe conditions are necessary to produce it at twin ends, and relatively lesser corroding conditions are necessary to produce it at grain interfaces. Thus the knife-edge attack is apparently a function of at least two major factors, one of which is the corroding condition and the other the degree of strain as related to the lack of registry. The absence of either of these factors would appear to preclude the possibility of knife-edge attack.

Further along these lines, as we have observed that the attack occurs to minimum degree where maximum registry exists, we must conclude that knife-edge attack at the edge of a carbide takes place on that face where maximum lack of registry occurs. Moreover, it is well known that the amount of strain which can exist in a lattice is limited by temperature or, more precisely, time at temperature. This limit is of no consequence at temperatures where atomic mobility is negligible and again the strain can be of no consequence at temperatures so great that the stress-relieving effect of the tem-

perature is almost instantaneous. However, at intermediate temperatures the time at temperature plays an important role and the degree of strain which can exist is a function of such time at temperature. In the case of stainless steel these intermediate temperatures encompass the range in which initial carbide precipitation and carbide growth take place, thus encompassing the range in which carbide precipitation is a factor giving rise to knife-edge attack. As a carbide forms and grows in registry such strain as may have existed at the interface, due to the adjacent grain, is relieved to some degree. As the carbide grows with lack of registry to the adjacent grain strain remains or is produced at the metal-carbide interface. When the precipitation temperature is sufficiently high, the stress-relieving effect is sufficiently rapid so that the strain in question is reduced during the time of precipitation. The net effect is a matter of rate. Thus the absence of knife-edge attack after precipitation temperatures greater than 1400 F may be accounted for in that the total remaining strain, even in the presence of lack of registry, is too small to provide the second factor essential to knife-edge attack. A similar argument may be applied using any other way of modifying energy levels. This concept may also help toward the understanding of another phenomenon. It is well known that some compositions of austenitic stainless steels show carbide precipitation and knife-edge attack after precipitation temperatures moderately different from those here cited, and there is reason to believe that here even the carbide forms may be precipitated at moderately different temperatures. This could well be related to the difference in change of energy levels occurring at such temperatures in stainless steels of somewhat different compositions.

To the scholar and the researcher the foregoing observations and hypotheses speak for themselves, but the engineer may well ask that frequently embarrassing question so tersely put in the current colloquial expression: "So what?" The 18 pct Cr-8 pct Ni stainless steels have filled an important need in many industries. The problem of carbide precipitation in these steels may be completely avoided. The columbium and titanium types are capable of eliminating this problem entirely, and the more recent extra low-carbon stainless steel with carbon less than 0.03 pct eliminates the problem for most applications. The utility of the foregoing therefore is not primarily directed toward solution of problems in the present chrome-nickel austenitic stainless steels but rather in the field which is just beginning to be developed—that of the new and more complex stainless steel compositions. This field encompasses the design of stainless alloys on the basis of a unified concept of their properties and behavior. To successfully attack such a design problem, broad understanding and a working concept are necessary. For example, the devising of new low-alloy engineering steels has been most successful and this is primarily due to the understanding and concept of hardenability as well developed in the past decade. In the design of new stainless steels the need for optimum corrosion resistance consistent with any given set of physical properties demands such a fundamental concept, particularly as the economic factor must also be satisfied. As the amount of stainless steel produced approaches the million ton per year mark, there arises the possibility of special stainless steels in large tonnage for more economical overall use, and it becomes imperative to design new grades for large specific fields of application. Typical are the steels with manganese and nitrogen playing an important role in the formation of the austenite. In these and other steels, a certain minimum amount of carbon will be present for technological or economic reasons. When that minimum amount is too great to avoid chromium carbide precipitation under some conditions this will, in some measure, limit the field of application of such steels. The observation and hypotheses given here should enable better planning for experimentation and new approaches to alloys for specific service requirements, and should lay the foundation for the advantageous manipulation of carbides in those steels which we may expect to fill large industrial areas in the not too distant future.

Summary and Conclusions

Although the observations in this study are such as to require judgment and therefore in general do not constitute positive proof of any of the following conclusions, they are sufficiently clear and sufficiently quantitative in nature so that conclusions in the following may be accepted as inferences with a very high degree of probability as to validity.

In the usual 18-8 type austenitic stainless steel with the carbon content somewhat greater than the limit of solid solubility, precipitation of chromium carbide Cr_4C and only that carbide occurs at temperatures and time consistent with atomic mobility. The carbide precipitate is essentially two-dimensional in character and its shape is determined by the degree of registry of atomic planes intercepting the interface. At grain boundaries, carbides are precipitated in the form of dendroidal plate-like leaves. At twin ends, they take the form of flat grids. At twin boundaries, they are flat triangles. At twin planes or other locations within the grain, they are primarily triangular and hexagonal plates. In annealed cold-rolled specimens subjected to precipitation treatment, the carbides are in the form of elongated leaves. All of this shows that the form of the carbide precipitate is a function of the nature and degree of registry of the lattice on either side of the interface in which the carbide forms.

Knife-edge attack by nitric acid or acidified copper sulphate solution never occurs at both sides of a precipitated carbide. It occurs only on the side of least registry, reflecting high interfacial energy. This could result from strain but could also be produced by other phenomena. Where time and temperature of precipitation are sufficient to allow stress-relieving or otherwise reduce lattice energy level on the less registered side of a carbide, there is no knife-edge attack adjacent to a carbide. Precipitation treatment for 100 hr at 1500 F is typical of such a time-temperature condition.

Elimination of knife-edge attack after all conditions of precipitation of the carbide is theoretically possible by providing suitable grain orientation. As yet we do not know how to accomplish this practically. However, it is hoped that the observations and hypotheses here given will enable better planning in experimentation to design new stainless steel compositions affording greater economy in large industrial fields of application.

Finally, we again hope that this presentation and dissertation is the type which Howe, himself, would have enjoyed.

Isothermal Mode of the Martensitic Transformation

by E. S. Machlin and Morris Cohen

The isothermal formation of martensite in a 71 pct Fe, 29 pct Ni alloy is found to take place mainly by the nucleation of new plates rather than by the growth of existing ones, and is dependent on the temperature and time of the isothermal hold, the amount of athermal martensite present, the state of internal strain, and the application of tensile stress. The conclusion is reached that the isothermal nucleation is activated by thermal fluctuations superimposed on localized regions of very high strain.

The reaction-path concept, involving martensite nucleation at strain embryos by athermal activation on cooling, or by thermal fluctuations on holding, reconciles the athermal and isothermal modes of transformation, and offers a unified picture of the kinetics of martensite formation.

THE phenomenon of isothermal martensite formation has been the subject of considerable study lately,[1] and its reality has been thoroughly established. The existence of such isothermal transformation has been claimed to confirm the nucleation and growth hypothesis as applied to the martensitic reaction.[2] However, the isothermal formation of a martensitic phase is also compatible with the reaction-path description of the transformation. The purpose of this investigation is to examine the isothermal mode of the martensitic reaction, both theoretically and experimentally, in order to test the likelihood of the above two mechanisms.

Material and Methods

The alloy used in this study contained about 71 pct Fe and 29 pct Ni. The complete analysis was 29.5 ± 0.2 pct Ni, 0.036 pct C, 0.02 pct N, 0.19 pct Mn, 0.09 pct Si, 0.008 pct P, and 0.006 pct S.

The amount of isothermal transformation was determined by electrical resistance measurements using a Kelvin double bridge. The specimens were in the form of rods 1/16 in. diam x 4 in. long. Austenitizing was performed at 1095 C for ½ hr either in a pre-purified nitrogen atmosphere or in an evacuated Vycor tube, followed by oil quenching to room temperature. After this treatment, the samples were completely austenitic, and the transformation studies were conducted at subatmospheric temperatures. Lineal analysis and X-ray determinations of retained austenite were used to calibrate the electrical resistance changes in terms of the percentage of martensite.

The martensite range curve for this alloy is given in Fig. 9 of ref. 6. The M_s temperature occurs at about −18 C (255 K).

Reaction-Path Theory

The nucleation and growth description of the martensitic transformation that occurs isothermally has already been given by Kurdjumow.[3] However, no comparable treatment exists using the reaction-path concept.[4] Consequently this section presents the reaction-path description of the isothermal mode of the martensitic transformation.

According to the latter theory, there is a reaction path (a strain) which describes the relative motion of the atoms during their transference from the austenitic to the martensitic state. The possibility exists, therefore, that the nucleation of a martensitic plate is accomplished by an embryo that comprises a state intermediate between that of austenite and martensite. This state may be attained within a finite volume by means of a homogeneous strain of the austenitic matrix. There is a free-energy barrier (F_a) along the reaction path, corresponding to a critical strain in a critical volume. When activation is achieved, a spontaneous increase in strain and volume of the embryo takes place to generate the full-size martensitic plate. This mode of nucleation is to be distinguished from the more conventional mode involving embryos of the martensitic phase that merely grow in size by an interface motion.

There are two ways whereby embryos in the austenitic phase can achieve the critical state of strain for isothermal nucleation: 1—through the formation of internal strains by plastic deformation or by stress; and 2—through thermal fluctuations, preferably superimposed upon existing internal strains. The activation free energy F_a must be supplied either mechanically by internal strains or thermally by energy fluctuations, or by a combination of both.

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Discussion on this paper, TP 3260E, may be sent, 2 copies, to AIME by July 1, 1952. Manuscript, Sept. 14, 1951. New York Meeting, February 1952.

This paper is based on a thesis by E. S. Machlin submitted in partial fulfillment of the requirements for the degree of Doctor of Science in Metallurgy to Massachusetts Institute of Technology, September 1950. The investigation was sponsored by the Office of Naval Research under Contract N5 ori 07814, Task No. XIV, Designation No. NR 031 142.

Fig. 1—Form of temperature dependence of the free energy of activation

When a localized region of internal strain (called a strain embryo) exists, the required free energy for activation is reduced by the amount of free energy F associated with the state of strain along the reaction path. (The strain must have the correct magnitudes along certain specified directions, or put more rigorously, the correct tensor nature.) Decreasing the temperature causes a reduction in F_a (Fig. 1) and athermally activated strain embryos to form martensite plates as soon as F_a equals the F associated with the most energetic strain embryos.

The probability per unit time of attaining the critical state by thermal fluctuations from any existing state can be approximated as in Appendix I. The initial rate of activation of embryos having free energies[1] between F and $F + dF$ at temperature T per unit untransformed volume is given by:

$$N_v f \exp\left[-\frac{F_a - F}{kT}\right] dF \qquad [1]$$

where $N_v\,dF$ = number of strain embryos with associated free energies between F and $F + dF$ at $t = 0$ per unit untransformed volume. N_v is therefore a distribution function which defines the number of embryos as a function of their energy at $t = 0$.

f = mean frequency of attempts to jump over barrier, sec^{-1}

F = free energy of activation, ergs

k = Boltzmann's constant, 1.380×10^{-16} ergs per °K

T = absolute temperature, °K

If N_v is assumed to be independent of F as a rough approximation,[2] it is found (Appendix II) that the initial rate of nucleation (per unit untransformed volume) of all embryos, not merely those having free energies between F and $F + dF$, is:

$$\left(\frac{dn}{dt}\right)_{\substack{t=0 \\ T=T_r}} = N_v f k T_r \exp\left[-\frac{F_a(T_r) - F_a(T_r)}{kT_r}\right] \qquad [2]$$

where $F_a(T_r)$ = free energy of activation at some precooling temperature T_r

$F_a(T_r)$ = free energy of activation at the isothermal reaction temperature T_r

$T_r < T_r$ and $F_a(T_r) > F_a(T_r)$

and the other quantities are defined as for eq 1. The purpose of the precooling treatment at T_r is to fix the initial amount of athermal martensite prior to the isothermal transformation at T_r. Thus, at the beginning of the isothermal transformation, the maximum free energy associated with the existing strain embryos is $F_a(T_r)$, all embryos of higher energy having been activated to form athermal martensite during the precool to T_r.

In order to convert the rate of activation of embryos to the rate of formation of martensite, the volume of martensite per embryo activated must be known. This quantity will decrease with increasing amounts of martensite because of the partitioning of the remaining austenite. However, important correlations can be derived from eqs 1 and 2 even without converting to transformation rates.

Table I. Effect of Temperature at Constant Athermal Martensite on Initial Rate of Isothermal Formation of Martensite

Precooling Temperature	Transformation Temperature	Initial Rate of Transformation Pct per Sec
[illegible]	[illegible]	[illegible]
[illegible] K	[illegible] K	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
200 K	200 K	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

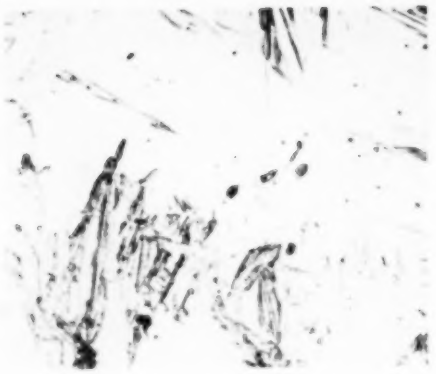

Fig. 2—Illustration of athermal and isothermal martensite in 71 pct Fe, 29 pct Ni alloy

Austenitic specimen was quenched to −25°C to produce athermal martensite and then was polished and etched with Marble's reagent at room temperature to reveal the martensite. Following this, the specimen was held at −25°C for 15 min during which isothermal martensite was formed. The specimen surface was then left untouched so that the isothermal martensite appears as upheavals. ×300

Correlation of Theory with Experiment

Nature of the Isothermal Transformation. According to the ideas just outlined, the major amounts of isothermal transformation should be provided by the nucleation of new plates rather than by the growth of existing plates. This follows from the fact that the reaction propagates with great speed once nucleated, and hence the nucleation rate should control the isothermal transformation process.

The isothermal transformation products are shown in Fig. 2 compared to the athermal transformation products. The specimen in question was quenched to −25°C to form athermal martensite,

Fig. 3—Temperature-time cycle for determining effect of temperature on isothermal transformation

then polished and etched at room temperature, and requenched to −25° C for 15 min. The specimen surface was then left untouched. Thus, the etched plates are the athermal products and the upheavals are the isothermal products. It was concluded from such observations that at least the major portion of the isothermal reaction occurs by the formation of new plates.

Effect of Temperature on the Initial Isothermal Rate of Transformation: The effect of temperature on the isothermal rate of transformation at zero time can be determined by subjecting specimens to the sequence outlined in Fig. 3. Several austenitic specimens are quenched to the same subzero reference temperature T_r to normalize the amount of athermal martensite, then each specimen is upquenched to one of the holding temperatures, T_h, and the isothermal rate of transformation is measured by electrical resistance changes.

A prediction can be made regarding the effect of temperature on the initial rate of transformation in such experiments. The quench to T_r within the martensitic range should yield a distribution curve of N_r vs. F as depicted in Fig. 4 which is the same for every specimen in this series. The volume of martensite formed per nucleus at the beginning of isothermal reaction is also the same in each specimen. Thus, the effect of temperature on the initial rate of transformation is indicated by eq 2. According to the exponent $\left[\frac{F_s(T_h) - F_s(T_r)}{kT_h}\right]$, it is possible that the initial transformation rate will first increase and then decrease with increasing temperature T_h. This will occur as a consequence of the temperature-dependence of F_s shown in Fig. 1. The temperature T_m corresponding to the maximum initial rate of transformation can be calculated (Appendix II) and the condition defining T_m is found to be:

$$\left.\frac{dF_s}{dT}\right|_{T_m} = k = \left[\frac{F_s(T_m) - F_s(T_r)}{T_m}\right] \qquad [3]$$

It is evident from eq 3 that T_m is dependent on the precooling temperature T_r. The maximum T_m for all possible values of T_r corresponds to $T_r = 0$ K.

Table I lists the measured initial rates of isothermal transformation for two different precooling temperatures. These rates are determined by measuring the slopes of the transformation-time curves at zero time. For $T_r = 78$ K (−195° C), the initial rates undergo a C-curve behavior with T_m occurring between 78° K (−195° C) and 203° K (−70° C). For $T_r = 203$° K (−70° C), the initial rates decrease monotonically with increasing temperature.

The temperature at which the maximum rate occurs can actually be calculated using eq 3. The procedure first involves a determination of the form of the F_s vs. T curve using the experimental data in Table I. The steps in the calculation are outlined in Appendix II and the result is presented in Fig. 5.***

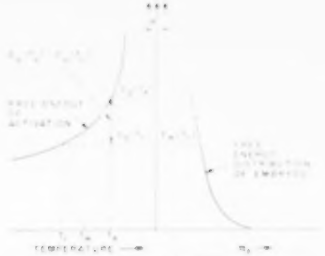

Fig. 4—Embryo energy distribution curve existing at start of isothermal transformation runs at temperature T_h after precooling to the lower temperature, T_r.

$F_s(T_r)$ is the maximum energy of the embryos remaining after the athermal transformation on cooling to T_r.

*** An assumption about the dependence of N_r on F must be made to solve the equations and the simplest assumption that N_r is independent of F was adopted here.

The form of the F_s vs. T curve derived from the data agrees with the expected curve shown in Fig. 1. The temperature of the maximum initial rate of isothermal transformation occurs where the slope is given by eq 3 and turns out to be about 150° K (−123° C) for $T_r = 78$° K. It is interesting to note that the relative activation free energy $[F_s(T) - F_s(78\text{ K})]$ at 203° K (−70° C) is only 535 cal per mol whereas at 253° K (−20° C) near M_s it is 2700 cal per mol.

If the curve in Fig. 5 is extrapolated to absolute zero, it can be shown that the T_m corresponding to $T_r = 0$ K is 160° K (−113° C). As previously indicated, this should be the highest T_m for all possible values of T_r. Therefore, if T_r is taken above 160° K, no T_m should exist. This accounts for the absence of a C-curve behavior for $T_r = 203$° K in Table I.

Time-Dependence of the Isothermal Martensitic Transformation: The course of the transformation as a function of time was measured at several different

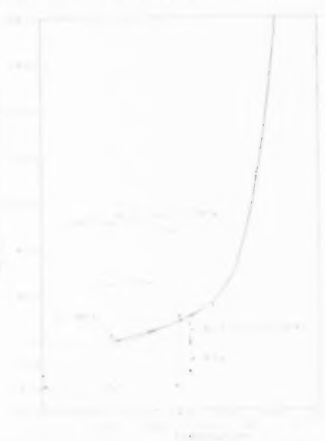

Fig. 5—Temperature-dependence of relative free energy of activation ($T_r = 78$ K). Graphical solution for T_m is illustrated.

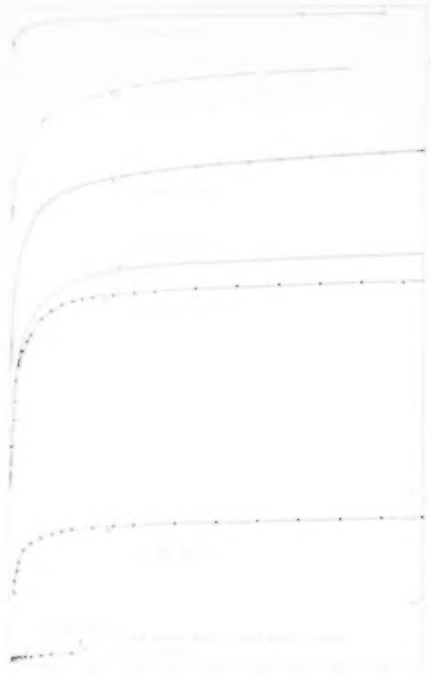

Fig. 6—Isothermal transformation subsequent to direct quench to temperatures shown
It should be noted that the amount of athermal martensite prior to the isothermal transformation increases with decreasing holding temperature.

temperatures and the results are plotted as percent martensite vs time in Fig. 6. The specimens were quenched directly from room temperature (austenitic state) to the indicated holding temperatures, and hence the amount of athermal martensite formed prior to the isothermal transformation was greater, the lower the holding temperature.

The time-dependence of the isothermal transformation does not obey a simple equation. It appears that the time function for this alloy is more complex than those obtained on other alloys.[7,8] The initial part of the transformation is very rapid compared to the marked retardation that takes place later (Fig. 6). This result may be a consequence of the fact that the reaction in the Fe-Ni alloy under study here tends to occur in bursts.[7] The bursts associated with the athermal transformation on cooling to the holding temperature probably set up a pattern of macrostresses, and when the reaction is subsequently nucleated via thermal fluctuations, it may be accelerated in regions of tensile stress,[7] thus accounting for the initial rapidity of the isothermal transformation. As the isothermal reaction proceeds, the macroscopic stresses may be expected to decrease until the remainder of the transformation occurs in the "normal" fashion that would be characteristic of "burst-free" transformations. For the "normal" transformation, it is possible to show quantitatively how the embryos are activated as a function of time (see Appendix III). The most energetic embryos are used up first, so that as time increases the free energy of the most energetic embryos remaining drops to lower levels.

The course of the isothermal transformation after some time at any given temperature depends on the state of the activating system at that time, i.e. the embryo-energy distribution relative to the activation energy at the temperature in question. A given state may be attained via a number of treatments, and the subsequent course of the transformation[9] at

[9] Neglecting the variation in martensite plate size due to the partitioning of the austenite.

the temperature in question should be independent of the treatment used to reach the given state. For example, suppose that a specimen is quenched to T_1 within the martensitic range, whereupon all embryos with associated energies greater than $F_a(T_1)$ are activated athermally. Then $F_a = F_a(T_1)$. If the specimen undergoes isothermal transformation to time t_1, it may be said that F_a is thereby lowered to F_a', and the subsequent course of the isothermal transformation can be recorded. However, it should be possible to reach the state characterized by F_a' by quenching another specimen to a lower temperature T_2 (where F_a is initially $F_a(T_2)$) and holding for some particular time t_2. It would then be expected according to the foregoing theory that upon upquenching from T_2 to T_1, the course of the subsequent isothermal reaction at T_1 would be the same as that previously observed after time t_1 when direct quenching to T_1 was conducted.[10] Two checks of

[10] The times t_1 and t_2 must not occur during the steep portions of the isothermal curves because the initial transient effects must be avoided if the predicted correlations are to be observed.

this prediction are given in Figs. 7a and b.

a—Dashed curve shows isothermal transformation at 213°K. Solid curve shows isothermal transformation at 203°K for 45 min, followed by isothermal transformation at 213°K. Plotted points are taken from the latter data, and are found to fit the form of the standard 213°K curve starting at 68 min.

b—Dashed curve shows isothermal transformation at 203°K. Solid curve shows isothermal transformation at 213°K for 80 min, followed by isothermal transformation at 203°K. Plotted points are taken from the latter data, and are found to fit the form of the standard 203°K curve starting at 45 min.

Fig. 7—Illustration of the equivalence of time and temperature on isothermal transformation.

Fig. 6—Temperature-time cycle for determining effect of thermal relaxation on isothermal transformation experiments.

In Fig. 7a, the isothermal curve at $T_1 = 203°K$ (−70°C) is interrupted at $t_1 = 45$ min by upquenching to $T_2 = 213$ K (−60°C). The subsequent isothermal transformation at 213 K is compared with the standard curve for this temperature, and is found to fit the form of this curve starting at $t_2 = 68$ min. Similar results were obtained with other combinations of T_1 and T_2 as listed in Table II where the corresponding times t_1 and t_2 are tabulated. The expected correlations are also found when the quenching sequence is reversed, except that the shift is to earlier times as expected. For example, in Fig. 7b, the isothermal curve at $T_1 = 213°K$ (−60°C) is interrupted at $t_1 = 80$ min by downquenching to $T_2 = 203°K$ (−70°C). The subsequent transformation curve at 203 K is found to fit the standard curve for this temperature starting at $t_2 = 45$ min.

The determination of the equivalent times t_1 and t_2 at temperatures T_1 and T_2 (Table II) permits the approximate evaluation of $[F_s(T_1) - F_s(T_2)]$. In Appendix III, it is shown that beyond some time t_0:

$$\frac{dF_s}{dt} = \frac{kT}{t} \qquad [4]$$

The interval t_0 is taken as the time required to activate one-half of the embryos at T having the free energy $F_s(T)$. Integrating eq 4 at T_1 and T_2 yields:

$$F_s(T_1) - F_{s_0} = kT_1 \ln \frac{t_1}{t_{0_1}} \qquad [5]$$

and

$$F_s(T_2) - F_{s_0} = kT_2 \ln \frac{t_2}{t_{0_2}} \qquad [6]$$

Subtracting eq 6 from eq 5, and assuming $T_1 \ln t_{0_1} = T_2 \ln t_{0_2}$:

$$F_s(T_1) - F_s(T_2) = kT_1 \ln t_1 - kT_2 \ln t_2 \qquad [7]$$

The calculated values of $N_v[F_s(T_1) - F_s(T_2)]$ based on eq 7 are given in Table II. Reasonably good agreement is found with the independent values based on the initial transformation rates (Fig. 5). The actual differences are probably due to the approximation involved in the derivation of eq 7. It is significant, however, that the same order of magnitude is obtained by both methods, and the results lend credence to the theory advanced here for the preferential using-up of embryos with time during the isothermal reaction.

It is also important to note that the isothermal transformation does not approach a limiting value, but appears to proceed indefinitely at a rate that decreases with time.[7] This characteristic is contrary to Kurdjumow's concept of temperature-dependent limiting amounts of isothermal transformation.[1] It is in agreement, however, with the concept of the consumption of embryos where the maximum energy-level of the remaining embryos drops at a rate that is inversely proportional to time. Furthermore, if the partitioning effect is small and N_v is assumed to be independent of F_s, eq 4 indicates that a plot of

Fig. 9—Isothermal transformation curves at −70°C after annealing at T_2 for 10 min and requenching to −70°C.

isothermal transformation vs. logarithm of time should be a straight line. This result has already been reported by Das Gupta and Lement.[7]

Effect of Heating Above M_s *on Subsequent Subzero Isothermal and Athermal Transformations:* If the embryos being activated during the isothermal transformation are regions of internal strain, then it might be possible to affect the course of the reaction by inserting a heating cycle during the hold at the subzero temperature. In order to check this interesting possibility, transformation experiments were conducted according to the cycles shown in Fig. 8. Austenitic specimens were quenched to −70°C, held for ½ hr while the isothermal transformation was recorded, then upquenched to various temperatures, T_2, for 10 min, requenched to −70°C and held at this temperature while the course of the subsequent isothermal transformation was measured. No transformation was observed during the 10-min hold at T_2. The effect of this relaxation††† treatment is shown in Fig. 9. Increasing temperature T_2 markedly lowers the rate and extent of subsequent isothermal transformation. The phenomenon is quite striking in that the relatively low "annealing" temperature of 60°C reduces the rate of isothermal transformation almost to the limit of detection (0.05 pct martensite in 3 hr).

††† The relaxation process may involve recovery or a migration of interstitial atoms to the strain centers.

In the light of these findings, it is evident that isothermal transformation cannot be nucleated in strain-free regions because such nucleation should go on irrespective of the treatments at T_2. Further, the embryonic regions must be very highly strained, otherwise relaxation at 0° to 60°C would be neg-

Table II. Equivalent Times at Temperature for Isothermal Transformation

T_1, °K		T_2, °K	t_1, Sec	t_2, Sec	$N_v[F_s(T_1) - F_s(T_2)]$, Cal
203	→	213	2700	4,680	340
203	→	223	3600	12,000	850
203	→	233	5600	~18,000	~1250
213	←	223	2120	4,800	385
203	←	213	2700	4,800	400

T_1, °K	T_2, °K	$N_v[F_s(T_1) - F_s(T_2)]$, Cal: Average from Equivalent Times	From Fig. 5	Difference Between 3rd and 4th Columns
203	213	370	180	190
203	223	800	535	265
203	233	~1250	895	~355

Fig. 10—Use of the N_v vs. F curve and T_s vs. F curves to illustrate effect of quenching, athermal transformation, and thermal relaxation

ligible. In other words, the martensite embryos in this alloy are inseparably associated with regions of extremely high internal strain. This conclusion was also reached in a study of the athermal transformation in the same alloy.[7]

The potent effect of annealing upon the subsequent rate of isothermal transformation may be called stabilization. Another experiment was performed in order to determine whether the stabilization required the existence of the athermal martensite. In this case, the initial quench to −70 C was interrupted at 60 C for 10 min after which the quench was continued to −70 C. The isothermal transformation curve obtained after this treatment was identical with that for no interruption at 60 C.[8] It

[7] The strain embryos in the austenite that start the athermal transformation are considered to be due to lattice imperfections. These are simply some defect in the austenite that the strains produced by the growth of martensite plates.

can be concluded, therefore, that the embryos stabilized at the T_s temperatures, corresponding to the curves in Fig. 9, were either produced by the athermal martensite or rendered more critical by the athermal martensite, or both. Probable forms of the embryo distribution function for the austenite state prior to transformation, for the state just after the athermal transformation, and for the state after relaxation are given in Fig. 10. The N_v vs. F curve after cooling to T_s in the martensitic range is drawn to show: 1—a reduction in F_m to the level of F_s (T_s) because of the athermal activation of all the higher energy embryos, and 2—an increase in the number of embryos at the remaining energy levels because of the strains set up by the athermal martensite.

As depicted in Fig. 10, the main effect of the stabilization is probably to reduce the maximum free energy of the existing embryos. It is expected that the F_m level after a given stabilization or relaxation treatment depends not only on the specific cycle but also on the F_m level prevailing prior to the relaxation cycle. A justification for this deduction is the fact that in cold-worked metals, the limiting value of a parameter such as yield strength after a long relaxation treatment increases monotonically with the magnitude of the yield strength prior to the relaxation treatment.[7]

With this picture of the effect of stabilization on the embryo distribution, it is possible to predict the dependence of the athermal transformation on stabilization. In the case illustrated by Fig. 10, a specimen is considered which has undergone athermal transformation on cooling to T_s. Suppose that a relaxation treatment is then introduced which lowers the F_m level from $F_s(T_s)$ to some lower value $F_s(T_s)$. Consequently, when the cooling is resumed, the athermal transformation will start at T_s, where $T_s < T_s$. This lowering of the resumption of the cooling reaction is a well-known characteristic of the stabilization phenomenon.[7] Moreover, if specimens are initially quenched down to different temperatures in the martensitic range and then subjected to relaxation treatments that produce about the same decrement in F_m, it may be expected that the ΔT required to restart the transformation on subsequent cooling will increase with decreasing temperature of the initial quench. This follows from the curvature of the F_s vs. T curve, and is exactly in line with the experimental facts.[7] Another feature that can be deduced is that, for a given amount of athermal martensite formed during the initial quench, the decrement in F_m due to relaxation will increase with the relaxation temperature, and therefore the athermal transformation on subsequent cooling should start at a lower temperature. This relationship is also observed experimentally.[7]

Further consequences of the above concepts are that stabilization should not occur to any appreciable extent at subzero temperatures where the rate of relaxation is nil; neither should it be measurable if the athermal transformation is interrupted in the region where the F_s curve is almost vertical because, then, a very large decrement in F_m would only correspond to a negligible difference between T_s and T_s (Fig. 10). Both these conditions probably hold true for the stabilization experiments of Barrett and Clifton[7] and thus an explanation is at hand for their inability to obtain definite stabilization effects.

Effect of Plastic Deformation Applied Above M_s on Subsequent Subzero Isothermal Transformation. In the previous section it was found that the anneal at 60 C before the quench to −70 C had no detectable influence on the isothermal transformation at −70 C, whereas a large stabilization effect was observed if the anneal was conducted after some athermal martensite was formed. From these results, it may be concluded that the athermal martensite probably produces new strain embryos which participate in the isothermal transformation, but which undergo relaxation at relatively low annealing temperatures. If this explanation is valid, the generation of strain embryos above M_s[2] by plastic deforma-

[2] M_d lies above M_s and is the temperature above which martensite does not form as a result of plastic deformation.

tion should lead to isothermal transformation even at temperatures where little or no athermal martensite is available to aid the isothermal nucleation process. Further, if the specimens are annealed after plastic deformation and prior to the isothermal hold,

Fig. 11—Effect of plastic deformation at 80 C in stimulating austenite to transform isothermally at −25 C

the extent of isothermal reaction should be smaller than in the as-deformed specimens.

Experiments were undertaken to check these expectations. Austenitized 1/16 in. diam rods were plastically deformed by wire drawing to 40 pct reduction in area at about 80° C. One deformed specimen was quenched to −25° C[11] within 15 min after deformation. Another deformed specimen was annealed in an evacuated Vycor tube at 200° C for 10 min, quenched to room temperature and then to −25° C.

[11] This temperature is above the M_s of a nondeformed specimen but slightly below the M_d.

The resulting isothermal reaction curves are given in Fig. 11. The nondeformed specimen undergoes negligible isothermal transformation at −25° C, whereas the deformed specimen exhibits a considerable amount of transformation, and the deformed and annealed specimen transforms at a reduced rate, as predicted. From the fact that the latter transformation is nevertheless appreciable, it may be deduced that the associated strain-embryo distribution function must exhibit larger values of N_v at all F levels, than that of the nondeformed specimen. Also, the athermal M_s should be higher for the deformed specimens than for the nondeformed specimen. This result was obtained in a separate series of experiments.

Effect of Applied Stress on the Isothermal Transformation: Predictions can also be made relative to the effect of stress applied at some time during the isothermal transformation upon the subsequent transformation characteristics. Let a given stress τ be applied to one specimen at time t_a, to another at t_b, etc., these times being measured at the isothermal transformation temperature T. The addition of this stress increases the free energy of the existing strain embryos (including those of maximum energy) by an increment $\Delta F(\tau)$. Now, according to eq 4, the effect of increasing the transformation time at temperature T from t_i to t_j is to decrease the effective maximum embryo energy by an amount:

$$\Delta F_m(t_i \rightarrow t_j) = kT \ln \frac{t_j}{t_i} \qquad [8]$$

and the corresponding "time-induced" nucleation is indicated by the area *dehi* in Fig. 12.

Similarly:

$\Delta F_m(0 \rightarrow t_i) = RT \ln \frac{t_i}{\tau_i} = I$, where I may be a function of temperature, and the corresponding nucleation is indicated by the area *cdij*.

For the case where:

$\Delta F(\tau) > \Delta F_m(0 \rightarrow t_i)$, the application of stress τ at time t_i at temperature T should raise F_m to above $F_v(T)$ as shown in Fig. 12. This relationship predicts that when the stress is applied, an amount of nucleation corresponding to the area *acjl* in Fig. 12 should occur simultaneously.[12] If the stress is applied at time t_k, then for the same reason the amount of nucleation corresponding to the area *bejk* of Fig. 12 should occur simultaneously.

[12] At the speed of formation of martensitic plates once activation has occurred.

Now there is an interesting property of the sum (ΣM) of the stress-induced and "time-induced" transformations that can be derived from a consideration of Fig. 12. It will be assumed that for small ΣM, the volume per martensitic plate formed is constant, that N_v is independent of F, and that all embryos activated produce martensitic plates. Under these conditions:

$$\Sigma M_{t_i} = K[\Delta F_m(0 \rightarrow t_i) + \Delta F] = K\Delta F(\tau)$$

$$\Sigma M_{t_j} = K[\Delta F_m(0 \rightarrow t_j) + \Delta F] = K\Delta F(\tau) \qquad [9]$$

$$\Sigma M_{t_k} = K[\Delta F_m(0 \rightarrow t_k) + 0] = K\Delta F(\tau)$$

or

$$\Sigma M_{t_i} = \Sigma M_{t_j} = \Sigma M_{t_k} \qquad [10]$$

and thus for $\Delta F(\tau) > \Delta F_m(0 \rightarrow t)$, ΣM should be independent of the time of application of the stress.

Whenever $\Delta F(\tau) > \Delta F_m(0 \rightarrow t)$, the predicted effect of applying a stress τ to the specimen is an increase in the isothermal rate of transformation without any simultaneous increment of stress-induced transformation. This is because the applied stress raises the level of F_m closer to $F_v(T)$ and thereby aids the thermal activation process, but a sudden increment of transformation should not occur because F_m (even with the applied stress) remains below $F_v(T)$ in this case. Also, since the ratio of the isothermal transformation rates just after to just before the stress application is:

$$\frac{\dot{p}_a}{\dot{p}_b} = \exp\left[\frac{[F_m(T) - [F_m + \Delta F(\tau)]]}{kT} - \frac{[F_m(T) - F_m]}{kT}\right]$$

then

$$\Delta F(\tau) = kT \ln \frac{\dot{p}_a}{\dot{p}_b} \qquad [11]$$

where $\dot{p}_a$ = transformation rate just after application of stress

$\dot{p}_b$ = transformation rate just before application of stress

$F_m + \Delta F(\tau)$ = maximum embryo free energy just after application of stress

F_m = maximum embryo free energy just before application of stress

Now if t_i equals the time when the stress is applied to produce the rate of transformation $\dot{p}_a$, there is some earlier time t_i at which the transformation rate

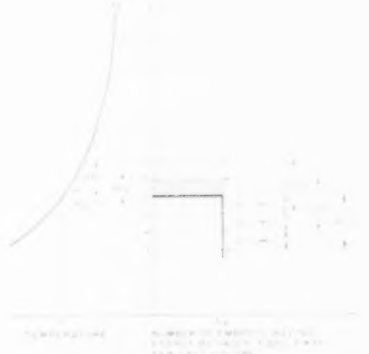

Fig. 12—Effect of stress τ applied after various times during isothermal transformation at temperature

Fig. 13—Effect of stress applied at various times on subsequent isothermal transformation at 78 K.

is also equal to $\dot{p}_0$ in the unloaded condition. According to eq 8

$$\Delta F_m(t_1 \to t_1) = kT \ln \frac{t_1}{t_0} \qquad [12]$$

Thus $\Delta F(t_1 \to t_1)$ is the decrement in the maximum embryo free energy as a result of the isothermal transformation from t_0 to t_1 during which the transformation rate decreases from $\dot{p}_0$ to $\dot{p}_1$ in the unloaded condition, whereas $\Delta F(\sigma)$ is the increment in the maximum embryo free energy as a result of the application of stress σ at time t_1 which increases the transformation rate from $\dot{p}_1$ back to $\dot{p}_0$. Accordingly, the equating of 11 and 12 gives

$$\frac{\dot{p}_0}{\dot{p}_1} = \frac{t_1}{t_0} \qquad [13]$$

An experimental check of the above predictions was made with $T = 78$ K (-195 C), $t_0 = 2$ min, $t_1 = 5$ min, $t_2 = 10$ min, $t_3 = 30$ min, and $\sigma = 32{,}600$ psi (elastic stress in tension). The results obtained are shown in Fig. 13. As predicted, the application of stress causes a sudden increment of transformation during the early stages of the isothermal transformation (1 under 10 min). Also ΔM is independent of time within the experimental error (a horizontal line can be drawn through the loci of the sum of the stress-induced martensite and the time-induced transformations). When the stress is applied after 10 min, however, there is no simultaneous increment of transformation, but the isothermal rate is increased as compared to the corresponding rate for the unstressed specimen. Finally a check of the data in Fig. 13 shows that

$$\frac{\dot{p}_0}{\dot{p}_1} = 9.3 \text{ and } \frac{t_1}{t_0} = 9.1$$

Therefore eq 13 is confirmed as well.

The above results constitute the strongest evidence, thus far, for the validity and usefulness of the reaction-path, strain-embryo concept of martensite formation.

Effect of Athermal Martensite on Initial Rate of Transformation. The amount of athermal martensite in the specimen should affect the subsequent rate of isothermal transformation for at least four reasons. 1—For a given number of embryos activated, the length (hence volume) of the plate will be smaller the larger the amount of prior martensite because of the partitioning of the remaining austenite. 2—The autocatalytic effect[7] in this alloy should increase with increasing amounts of prior martensite up to amounts where the number of "free" ends[8] of the plates (ends which are surrounded by austenite) become negligibly small (estimated from micrographs as about 20 pct). 3—The process by which increasing amounts of martensite are obtained can only result in decreasing the maximum energy associated with the remaining strain embryo distribution. 4—As the transformation proceeds, the decreasing amount of austenite will also reduce the rate of transformation. To summarize, among the above four factors, only the catalytic effect of the athermal martensite may be expected to increase the rate of isothermal transformation, and this only up to about 20 pct of prior martensite. For amounts larger than about 20 pct, a substantial decrease in the rate of isothermal transformation is anticipated.

The experiments to check these predictions were performed by quenching austenitic specimens to a series of subzero temperatures for 1 min at temperature, then upquenching to a holding temperature of -40 C and following the course of the isothermal transformation. The results in Fig. 14 show that the rate of isothermal transformation increases with the amount of prior (athermal) martensite up to about 20 pct. Also a decrease in the rate of isothermal transformation is obtained with increasing amounts of athermal martensite beyond about 20 pct.

[8] The austenite regions at the ends of martensitic plates are found to act as preferential nucleation sites for the formation of additional plates.[7]

Significance of Results

It has been demonstrated that the reaction-path theory, involving nucleation at strain embryos by superimposed thermal fluctuations, is entirely consistent with the isothermal mode of the martensitic reaction. In fact, this theory offers a common basis for understanding the two modes of the martensitic reaction. It has been possible to predict results with respect to the athermal transformation knowing the isothermal transformation behavior, and vice versa. This success of the reaction-path theory attests to its likelihood.

It is now equally clear that if any other types of embryos are postulated for the martensitic transformation, they must be inseparably associated with regions of high internal strain. The nucleation and growth theory proposed by Kurdjumow and Maksimova[9] does not take this factor into account, although these investigators do come to the conclusion that the martensite nuclei are "formed in certain special regions."

The quantitative form of the nucleation and growth theory of Kurdjumow and Maksimova differs mainly in one respect from the equations presented in this paper. However, this difference is fundamentally important and arises from their use of an activation energy for growth, U:

$$\left(\frac{dn}{dt}\right)_{t=0} = K \exp\left[-\frac{W+U}{kT}\right] \qquad [14]$$

which is absent from eqs 1 and 2 of this paper. W is the free energy of activation for nucleation and decreases with decreasing temperature. The quantity U is taken to be temperature-independent, and corresponds to the activation energy required to transport an atom from the austenite side to the martensite side of the interface between the two phases.[9] If eq 14 correctly represents the facts. In this con-

cept, U would also be the activation energy for growth of the nucleus to the final plate. On the other hand, if the transformation is propagated as a strain wave[10] the activation energy for growth should be virtually zero neglecting fractional effects.

A critical experiment was conducted to differentiate between these two viewpoints. At decreasing temperatures below T_o, the initial rate of isothermal transformation decreases and becomes nil at sufficiently low temperatures. According to the Kurdjumow-Maksimova nucleation and growth theory,[7] this retardation of the reaction rate with decreasing temperature is due to the concomitant decrease in the growth rate. At such low temperatures, the factor $\exp\left[-\frac{U}{kT}\right]$ is supposed to control the reaction rate because W becomes very small and the factor $\exp\left[-\frac{W}{kT}\right]$ approaches unity. However, according to the reaction-path theory, the retardation is due to the decreased rate of activation of strain embryos, with the rate of growth of the activated embryos still occurring at a velocity approaching that of an elastic wave. Now, if a stress is applied to a specimen at a temperature like 4 K where the rate of isothermal transformation is nil, the nucleation and growth theory predicts that no additional transformation should occur because, even though new nuclei may be formed by the deformation, the growth rate of such nuclei would be too small to yield a measurable increase in the amount of martensite. On the other hand, the reaction-path theory predicts the likelihood of stress-induced transformation even at 4 K because the nuclei can grow rapidly to full size plates, as soon as the activation is accomplished by the applied stress.

The 71 pct Fe, 29 pct Ni alloy was found to contain about 13 pct austenite on cooling to 4 K (−269 C) and no isothermal transformation was detected on holding. Yet, when stress was applied at this temperature, transformation took place simultaneously as evidenced by audible clicks. Moreover, after about 7 pct elongation, less than 1 pct austenite remained. These findings demonstrate unequivocally that the nucleation and growth theory does not correctly represent the growth aspect of the isothermal martensitic transformation, while the reaction-path theory is consistent with the observations. Similar results have been found with 18-8 stainless steel.[9]

Another issue lies in the interpretation of the temperature-dependent factor W of eq 14 or $(F_n - F)$ of eq 1. According to eq 14, this factor is the free energy required to form a nucleus starting from strain-free austenite, whereas according to eq 1 it is the difference between the free energy to form a nucleus and the existing free energy associated with a given embryo. The results of this research confirm the strain-embryo concept and show that nucleation from strain-free austenite is highly unlikely. Further, it is not possible to obtain athermal (time-independent) transformation according to the nucleation and growth, eq 14.88 whereas the reaction-path theory indicates that this possibility exists. Eq 14 demands that the M_s temperature should decrease at an increasing rate as the cooling rate is increased, in C-curve fashion. The high-speed quenching experiments of Esser et al.,[11] Greninger,[3] and Duwez[12] offer definite evidence that this is not the case. In fact, the well-recognized athermal feature of the transformation has been taken into account by other proponents of the nucleation and growth theory for martensite formation,[13] and they have altered the theory to an athermal nucleation and growth concept.

[10] This equation indicates that time is required at any temperature to form a finite number of nuclei.

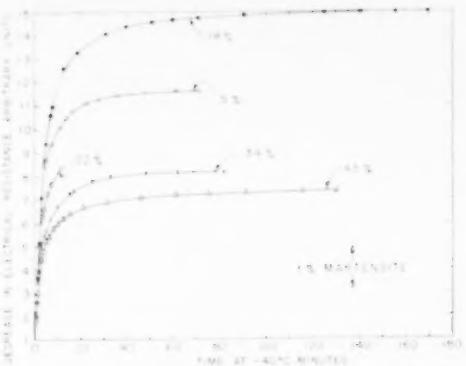

Fig. 14—Effect of athermal martensite at start of test on subsequent isothermal transformation.

The reaction-path theory explains the simultaneous existence of the insuppressiblity of the martensitic reaction and its isothermal mode as follows. If F_m is the maximum free energy of a strain embryo distribution existing in the austenite, the nucleation will occur during rapid cooling as soon as a temperature is reached where $F_m = F_a$, the activation free energy. No thermal fluctuations are necessary for nucleation in this case, and because of the high rate of propagation after nucleation, the transformation is found to be insuppressible.

On the other hand, when athermal transformation has occurred on cooling down to a given temperature T, and all the strain embryos with energy greater than $F_a(T)$ have been activated (whether they existed in the original austenite or were produced by the athermal transformation) then thermal fluctuations superimposed upon the remaining embryos can and do cause isothermal nucleation. This mode of nucleation is time-dependent and hence is suppressible by rapid cooling.

Notwithstanding the necessity for thermal fluctuations in the isothermal transformation, the strain embryos produced by the athermal martensite may play a major role. If no athermal martensite is formed or if it is stress-relieved after forming, isothermal activation through thermal fluctuations is much less probable although still possible. By the same token, the isothermal nucleation may be aided by prior plastic deformation or by tensile stress applied during the run.

It might appear from the foregoing that the isothermal transformation should be found more generally in martensitic systems, but actually the necessary conditions are somewhat critical. In the first place, at ordinary temperatures and above, relaxation of the more energetic embryos takes place, and this makes nucleation by thermal fluctuations more difficult despite the higher temperatures involved. Second, the amount of isothermal transformation

may be quite small, requiring extremely sensitive techniques for detection. Third, at temperatures near M_s the F_a vs. T curve may be quite steep so that the temperature control during holding would have to be exceedingly precise in order to prevent athermal increments of transformation from markedly reducing the maximum energy of the embryos available for the isothermal transformation. These circumstances lead to maximum isothermal reactions in the vicinity of −120° C for the alloy under study here.

Another feature of the transformation that should be considered is the possibility of obtaining an apparent suppression of the martensitic reaction. This reported result of Kurdjumow and Maksimova can be explained using the reaction-path concept. It is conceivable that in some alloys, the activation energy for all temperatures will be larger than the maximum of the existing embryo-energy distribution. Then the alloy can be quenched even in the vicinity of absolute zero without athermal transformation. However, on reheating to a temperature in the neighborhood of T_0 (Fig. 5) where the thermal fluctuations are more potent, it is possible that isothermal nucleation will occur even though no athermal martensite had previously formed. The authors have not found this combination of factors in any of the alloys studied to date, but if Kurdjumow and Maksimova's suppression experiments are taken at face value, the above explanation would account for their result. In other words, perhaps the athermal transformation did not occur in their experiments because of the particular relation of the free energy of activation to the embryo distribution available in the austenite, and should not be regarded as having been suppressed by the rapid cooling.

However, allowing time for the influence of thermal fluctuations may permit isothermal transformation in a suitable temperature range, and this is what can be suppressed by the rapid cooling. According to the above principles, it becomes evident that the relative importance of the isothermal compared to the athermal mode of martensitic transformation may range between wide limits from one alloy system to another.

Conclusions

1—The isothermal rate of martensite formation in a 71 pct Fe, 29 pct Ni alloy is dependent upon the temperature and time of the isothermal hold, the amount of athermal martensite present, the state of internal strain, and the application of tensile stress.

2—The isothermal transformation takes place primarily by the nucleation of new plates rather than by the growth of existing ones.

3—The conclusion is reached that the isothermal nucleation process is activated by thermal fluctuations superimposed on localized regions of a very high strain. These strain embryos may be produced by the formation of athermal martensite or by plastic deformation of the austenite, and can be relaxed by annealing at comparatively low temperatures. The strain embryos in the original as-cooled austenite which account for the start of the athermal transformation do not materially aid the isothermal reaction in this alloy, but this possibility is not ruled out for other systems.

4—The relaxation of strain embryos produced by the athermal transformation results in the stabilization of both the athermal and isothermal modes of transformation, and accounts for the stabilization phenomena observed in plain carbon and low alloy steels.

5—The form of the activation energy vs. temperature curve has been established, based on the reaction-path theory. The theory predicts that in the presence of a given amount of athermal martensite, the initial rate of isothermal transformation should be a maximum at a certain holding temperature. This is confirmed by experiment.

6—Quantitative relationships between the isothermal and stress-induced transformations have been derived, and checked experimentally.

7—The reaction-path concept, involving nucleation at strain embryos by athermal activation on cooling or by thermal fluctuations on holding, provides the relationship between athermal and isothermal martensite formation, and offers a unified picture of the kinetics of the transformations. In principle, the isothermal reaction is suppressible by rapid cooling while the athermal reaction is not. Yet the possibility exists that, in some alloys, the maximum energy of the strain embryos may not be sufficient to activate the transformation athermally. In this case apparent suppression may occur.

8—The nucleation and growth theory of Kurdjumow and Maksimova does not predict any athermal transformation and is therefore inconsistent with one of the main features of the martensitic reaction. It also does not correctly represent the growth aspect of the isothermal transformation.

Acknowledgments

The authors are indebted to William R. Yankee who rendered effective assistance in many phases of this work. They also wish to acknowledge the financial support of the Office of Naval Research. The International Nickel Co. kindly supplied the Fe-Ni alloy that formed the basis of this investigation.

Appendix I
Derivation of Rate Equations

Let the number of embryos with free energies between F and $F + dF$ just after the quench to temperature ($t = 0$) be given by $N_0 dF$. (These embryos may be formed mainly by the athermal martensite transformation.) After a time t suppose that $n_0 dF$ of these embryos have been activated so that the number of embryos of this energy remaining is $(N_0 - n_0)dF$. Then the rate of activation of these embryos is:*

$$\frac{d\,(n_0 dF)}{dt} = (N_0 - n_0)\, f \exp\left(-\frac{F_a - F}{kT}\right) dF \quad [A\text{-}1]$$

where f = mean frequency of attempts to jump over barrier, sec^{-1}

F_a = free energy of activation, ergs

k = Boltzmann's constant, 1.38×10^{-16} ergs per °K

T = absolute temperature, °K

The solution of eq A-1 is:

$$n_0 dF = N_0 \left[1 - \exp\left\{-ft \exp\left(-\frac{F_a - F}{kT}\right)\right\}\right] dF \quad [A\text{-}2]$$

as can be verified by differentiating with respect to time and substituting in eq A-1.

At $t = 0$, $n_0 = 0$ and:

$$\left[\frac{d\,(n_0 dF)}{dt}\right]_{t=0} = N_0 f \exp\left(-\frac{F_a - F}{kT}\right) dF \quad [A\text{-}3]$$

This is eq 1 in the text.

* This is the usual approximation that neglects the probability of the free energy reaching a value larger than F_a by fluctuations. The energy density of embryos as a function of their energies is given by the distribution function $N_0 = n_0 dF$ at any time t and N_0 at $t = 0$.

Appendix II

Calculation of $\dot{p}$ vs. T

In order to analyze the data to determine F_c it is necessary to make an assumption concerning the dependence of N_c on F. The simplest assumption is to take N_c independent of F.[1] Also it is desirable to use the initial rate of transformation to eliminate any effects of relaxation. On integrating eq A-3 to sum up the initial rate of activation of all the embryos, the initial rate of nucleation per unit untransformed volume of a specimen at T_c after having been previously cooled to T_r (see Fig. 4) is:

$$\left(\frac{dn}{dt}\right)_{\substack{t=0\\T=T_c}} = N_c f \int_0^{F_c(T_r)} \exp\left(-\frac{F_c(T_c)-F}{kT_c}\right) dF$$

$$= N_c f kT_c \left[\exp\left(-\frac{F_c(T_c)}{kT_c}\right)\right] \left[\exp\left(+\frac{F_c(T_r)}{kT_c}\right) - 1\right] \quad [A\text{-}4]$$

where $F_c(T_r)$ is taken to be the maximum energy of embryos remaining after the precool to T_r, all those of higher energy having been activated to athermal martensite during the precool.

Let us assume $\frac{F_c(T_r)}{kT_c} \gg 0$, then eq A-4 becomes:

$$\left(\frac{dn}{dt}\right)_{\substack{t=0\\T=T_c}} = N_c f kT_c \exp\left[-\frac{F_c(T_c)-F_c(T_r)}{kT_c}\right] \quad [A\text{-}5]$$

which, under the conditions at hand, is proportional to the measured isothermal transformation rate at $t = 0$ and $T = T_c$. At $T = T_r$:

$$\left(\frac{dn}{dt}\right)_{\substack{t=0\\T=T_r}} = N_c f kT_r \quad [A\text{-}6]$$

From the ratio of eqs A-5 to A-6:

$$\ln\left[\frac{\text{initial transformation rate at } T_c}{\text{initial transformation rate at } T_r} \cdot \frac{T_r}{T_c}\right] = \frac{F_c(T_c)-F_c(T_r)}{kT_c} \quad [A\text{-}7]$$

The free energy difference $[F_c(T_c) - F_c(T_r)]$ can be determined as a function of T_c from eq A-7. The quantity $N[F_c(T_c) - F_c(T_r)]$ is plotted in Fig. 5 vs. T_c, where N is Avogadro's number. The enthalpy and entropy of activation are both functions of temperature in these considerations.

Derivation of Temperature for Maximum Initial Rate of Isothermal Transformation: From eq A-5, the initial rate of nucleation at any temperature T after precooling to T_r ($T < T_r$) can be written:

$$\left(\frac{dn}{dt}\right)_{\substack{t=0\\T=T}} = \text{constant } T \exp\left[-\frac{F_c(T)-F_c(T_r)}{kT}\right] \quad [A\text{-}8]$$

Under the conditions of the experiment, the initial rate of isothermal transformation is:

$$\left(\frac{dp}{dt}\right)_{t=0} = \dot{p} = C\left(\frac{dn}{dt}\right)_{t=0} \quad [A\text{-}9]$$

where p is the volume fraction of martensite related to a unit volume of the alloy, and C is a constant because at each holding temperature the initial transformation occurs in the presence of the same quantity of athermal martensite.

If $\dot{p}$ is now differentiated with respect to T and the result set equal to zero, this will determine the temperature, T_m, which makes $\dot{p}$ a maximum or a minimum, whence:

$$\left(\frac{dF_c(T)}{dT}\right)_{T_m} = k = \frac{F_c(T_m)-F_c(T_r)}{T_m} \quad [A\text{-}10]$$

This is the criterion for the maximum initial rate of transformation since it can be shown that $\frac{d^2\dot{p}}{dT^2} < 0$.

The method for obtaining $[F_c(T) - F_c(T_r)]$ as a function of T was presented earlier in this Appendix. The slope of this curve is equal to $\frac{dF_c(T)}{dT}$ since $F_c(T_r)$ is held constant. The value of T_m satisfying eq A-10 can be solved graphically by trial and error starting with $\frac{dF_c(T)}{dT} = k$ as the first approximation. The second or third approximation is usually sufficient. In this way, T_m corresponding to Fig. 5 was found to be 150° K (−123° C).

If $N_c[F_c(T) - F_c(T_r)]$ is plotted vs. T, then A-10 becomes:

$$\left(\frac{d[N_c F_c(T)]}{dT}\right)_{T_m} = \frac{RT_m + N_c[F_c(T_m) - F_c(T_r)]}{T_m} \quad [A\text{-}11]$$

where R is the gas constant. These quantities are indicated in Fig. 6.

Appendix III

Calculation of $\frac{dT}{dt}$

Let the free energy of embryos corresponding to a given value of the ratio $\frac{n_c}{N_c} = K$ be designated as F_c. n_c and N_c are defined as in Appendix I, and K represents a certain fraction of embryos of energy F_c that have been activated during isothermal transformation at temperature T. The problem is to determine the time-dependence of F_c, keeping K constant. This can be done as follows:

1—Divide eq A-2 by $N_c dF$ and set the ratio $\frac{n_c}{N_c} = K$.

2—Differentiate the resulting equation with respect to time.

$$\frac{d}{dt}(K) = 0 = \frac{d}{dt}\left\{1 - \exp\left[-ft \exp\left(-\frac{F_m - F_c}{kT}\right)\right]\right\}$$

$$= \exp\left[-ft \exp\left(-\frac{F_m - F_c}{kT}\right)\right]$$

$$\left[ft\left[\exp\left(-\frac{F_m - F_c}{kT}\right)\right]\frac{1}{kT}\frac{dF_c}{dt} + f\exp\left(-\frac{F_m - F_c}{kT}\right)\right] \quad [A\text{-}12]$$

Fig. 15—Dimensionless representation of embryo energy distribution curve as a function of time

Because the first brace cannot equal zero, then the latter brace can be set equal to zero and it is found that

$$\frac{dF_c}{dt} = \frac{kT}{t} \qquad [A\text{-}13]$$

The graphical interpretation of eq A-13 is given in Fig. 15, from which it is evident that the first effect of time is to change the form of the embryo distribution curve in the region of the highest energy embryos. The initial horizontal plateau becomes a sloping plateau. Thereafter, the shape of the embryo distribution curve is practically unchanged, except for a lowering of the height (energy) of the "plateau" at a rate that is inversely proportional to the time at temperature. This signifies that the highest energy embryos tend to be consumed first in the transformation.

It is convenient to define a single parameter to describe the sloping plateau. The value $K = \frac{1}{2}$ defines an "average" height of the plateau that is equivalent to the horizontal plateau $F_c(T)$ obtained just after direct quenching to T (Fig. 4). The free energy associated with this "average" height can thus be denoted as F_m during the isothermal transformation. The rate of decrease of F_m with time is merely a specialized case of eq A-13, namely

$$\frac{dF_m}{dt} = \frac{kT}{t} \qquad [A\text{-}14]$$

It is important to realize, however, that eq A-14 applies only after a time t_c, which is the time required for one-half the embryos having the free energy $F_c(T)$ to be activated. Using eq A-2, and noting that $F = F_m - F_c(T)$ in this case

$$t_c = \frac{1}{\tau} \ln \frac{1}{2} \qquad [A\text{-}15]$$

An approximate relation can now be derived for the time-dependence of the transformation beyond the time t_c. If it is assumed that N_1 is independent of F and that the effect of partitioning of the austenite by the martensitic plates formed isothermally can be neglected, then the amount of transformation, p, appearing isothermally during time t is proportional to the number of embryos that have been activated. This, in turn, is proportional to the attendant lowering of the maximum embryo energy from $F_c(T)$ to some value F_m. Thus

$$p = C \left| F_c(T) - F_m \right| = C \int_{t_c}^{t} \frac{kT}{\tau}\, dt =$$

$$Ck\,T \ln \frac{t}{t_c} \quad \text{for } t > t_c \qquad [A\text{-}16]$$

Under the assumptions involved, eq A-16 predicts that the percentage of isothermal martensite should increase linearly with the logarithm of time.

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Recrystallization of Aluminum Single Crystals After Plastic Extension

Recrystallization of aluminum single crystals after plastic extension is carefully studied in relation to the structure of the deformed matrix. The shapes of the new grains are analyzed with regard to slip planes and to the presence or absence of deformation bands. A mechanism by which the orientations of the recrystallized grains are related to the parent lattice is described.

EXPERIMENTS previously reported[1] have been extended to develop some of the characteristics of the new crystals which are formed on annealing axially strained crystals whose deformational characteristics had been documented with special care. Thus, the presence of deformation bands affects the growth contours of the crystals, some of the strained crystals produced single crystals anew, and some, polycrystals, on annealing, while others merely "recovered" or "polygonalized" after the 600° C annealing treatment generally adopted in these tests.

In the matter of orientational relationships between new crystals and the strained matrix, the present experiments have added little to previous experience, which had demonstrated great variety in the range of orientations encountered and no simple theory or correlation. For example, there has been ample evidence for the predominance in various face-centered cubic metals of a favored orientational relationship, viz., a rotation of 30° to 40° around a <111> axis, between grains growing in a matrix with a strong single orientation texture and the matrix itself.[1-5] This reorientation has been interpreted by various investigators in support of both the "oriented nucleation" and the "oriented growth" hypothesis.

In the case of axially extended single crystals of aluminum, no general relationship, such as the one stated above, can be used to correlate the orientations of the recrystallized grains with that of the original crystal. Thus, Carpenter and Elam[6] and Burgers and Basart[7] were content to assume that the orientational relationships so developed were random in nature. Mathewson, however, in the Campbell Lecture of 1943[8] argued on the basis of <112> slip that a complex strain, chiefly characterized by rotation around a variable axis in the slip plane combined with a principal rotation around the pole of the slip plane, could be responsible for such devious relationships. Nevertheless, owing to the limited data now available dealing with orientational relationships between new grains and the single crystals strained in tension from which they have recrystallized, no adequate examination of the above generalization could be made. Here, there is the disturbing preliminary condition that any desired orientational relationship may be expressed by means of two rotations about mutually perpendicular axes, so the process lacks a certain critical flavor and any successful choice of axes meeting certain theoretical requirements could be replaced by another differently selected pair.

With this reservation clearly in mind the process of double rotations, as previously indicated, was used to relate the orientations of the single crystals which grew out of the strained single crystalline matrix and was construed as certain evidence in favor of the theory of incongruent shearing action proposed by Mathewson[8] as a necessary element in the {111} slip process with close-packed metals. There is here

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Discussion on this paper, TP 3291E, may be sent, 2 copies, to AIME by July 1, 1952. Manuscript, May 31, 1951; revised, Feb. 6, 1952. New York Meeting, February 1952.

This paper represents part of a thesis by N. K. Chen submitted in partial fulfillment of requirements for the degree of Doctor of Engineering to the Graduate School of Engineering, Yale University, May 1950.

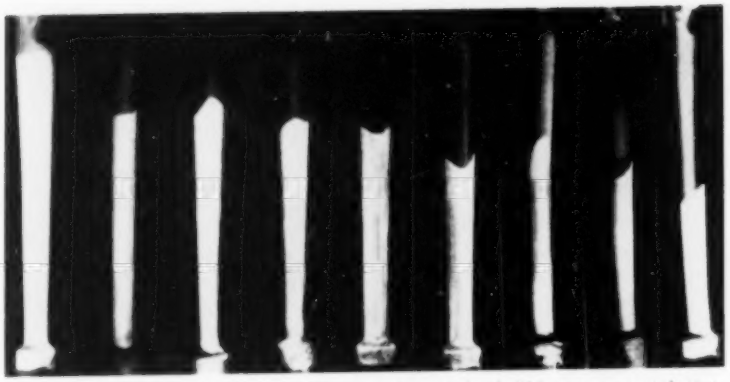

Fig. 1—Crystal growth in specimen A-4. Taken after the third, fourth, fifth (two views), sixth (two views), eighth (two views), and ninth (600 C) anneals, respectively. X1. Area reduced approximately 70 pct for reproduction.

the simplified observation that one of the octahedral slip planes (primary, conjugate, or cross) of the strained matrix is relatively close to a (corresponding) plane in the new crystal, so that whatever the theoretical implication of its reorientation, this can be represented by a single rotation. It was also considered worthy of note that the second rotation, now around this relocated [111] pole, which completes the pattern of reorientation, bears a resemblance to that required by Kronberg and Wilson,[1] in their use of coincidence sites to show the possibility of comparatively large reorientations by small atom displacements, perhaps activated by residual lattice strain due to prior deformation. Since the present analysis is based on strain-hardened material, instead of previously annealed material undergoing secondary recrystallization, the theoretical rotations predicted by Kronberg and Wilson would be subject to a more or less pronounced deviation.

It is believed that this method of exhibiting the relationship between new crystals and the strained matrix, according to the enlarged description under the heading, Orientational Relationships, of the included projections and tabular material, is sufficiently direct and comprehensive to permit eventual independent study of the factual material presented in this part of the paper, quite apart from the theoretical interpretation preferred by the authors.

Experimental Procedure

Twelve tapered aluminum single crystals were annealed after previous extensions. The designation and history of each crystal are shown in Table I. All crystals except A-3 were annealed at 600 C for different periods of time, continuously or intermittently, up to the total time indicated in the table. Cumulative heat treatment was carried out on A-3 following the schedule given in Table II. Aqua regia was used as a macroetching reagent. The orientations of new grains were determined from back-reflection Laue X-ray photograms. They were then plotted in the same relationship to the X-ray beam as that of the deformed crystal from which they grew. Each of seven crystals had formed only one visible new crystal during the annealing process, and the isothermal growth of such crystals was followed. Two crystals did not recrystallize (or recrystallized "in situ") and the remaining three specimens formed polycrystals.

Growth Characteristics of New Crystals

Stages of growth in one of the seven crystals, A-1, A-1', A-4, A-5, A-16, A-18, and A-20, which formed

Table I. General Summary of Recrystallization Data from 12 Tapered Aluminum Single Crystals

Crystal No.	Elongation	Shear	Deformation Band	Total Time of Anneal, Hr	Total Time of Anneal, Min	Recrystallization Product
A-1	1.24–1.55	0.059–0.96	No	2	00	Single crystal (A-1')
A-1	1.55–1.94	0.52–0.62	Yes	23	00	Single crystal (A-1') with unrecrystallized matrix
A-2	4.19–6.00	0.057–0.90	Yes		00	Unrecrystallized
	12.2–9.80	1.01–0.20			00	Polycrystals
	(Second extension)					
A-3	11.10–5.40	0.20–0.14	No	*		Polycrystals
A-4	1.22–1.32	0.056–0.096	No	6	45	Single crystal (A-4')
A-5	2.47–2.49	0.140–0.060	No	3	15	Single crystal (A-5') with 2 tiny crystals at the shoulder
					20	Polycrystals
A-6	56.5–9.81	0.90–0.29	Yes			
	Neck drawn					
A-15	1.90–2.00	0.10–0.00	Yes	24	00	Unrecrystallized
A-16	1.42–1.32	0.09–0.01	Yes	24	00	Unrecrystallized
A-18	2.45–2.45	0.52–0.07	No		00	Single crystal (A-18')
A-19	14.4–5.30	1.04–0.51	Yes	3	00	Single crystal (A-19')
A-20	4.8–1.00	0.84–0.012	Yes	22	00	Single crystal (A-20') with some unrecrystallized matrix and one tiny grain at the shoulder

* Cumulative heat treatment was carried out on crystal A-3 following the schedule of time and temperature given in Table II.

only one active nucleus during the isothermal annealing process at 600 C, are shown in Fig. 1. (A-3 and A-20 produced one small grain at the shoulder). With the occurrence of recrystallization, the length of the new grain was measured in a direction parallel to the axis of the specimen along eight different elements around the circumference of the crystal. The average value of these lengths was then taken from each series of measurements and plotted against time of annealing, Fig. 2.

The growth contours of the new crystal at different stages were plotted, as represented in Fig. 3, for crystal A-4, in the form of "developed" curves.*

* In engineering drawing, the operation of laying out the true-scale surface on one plane is called the "development" of the surface.

It was noted that the boundaries of the new crystal in A-4 could best be related to the primary slip plane on one side and conjugate slip plane diametrically opposite. Similar analysis of other crystals seemed

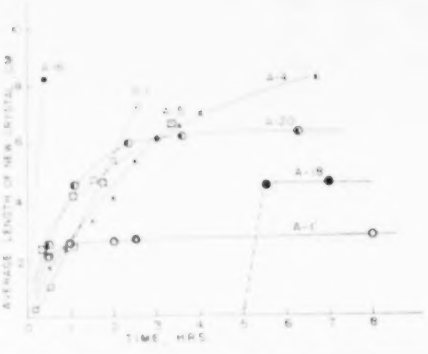

Fig. 2—Length of new grains formed during recrystallization vs. time of numbered specimens at annealing temperature, 600 C.

Table II. Cumulative Annealing Schedule for Crystal A-3
Shear, 0.33-0.14

Temperature, °F	Time, Min	Inspection
150	10	No recrystallization
185	10	No recrystallization
225	10	No recrystallization
265	10	No recrystallization
295	10	No recrystallization
305	10	No recrystallization
325	10	No recrystallization
335	10	No recrystallization
345	20	No recrystallization
355	20	No recrystallization
365	20	No recrystallization
385	20	No recrystallization
420	20	No recrystallization
450	20	No recrystallization
475	20	Recrystallization observed up to the position, shear, about 0.28
500	20	Some growth of old grains and formation of new grains around shear, 0.25
520	20	More new grains formed up to shear, 0.23
540	20	More new grains formed up to shear, 0.21
560	20	More new grains formed up to shear, 0.19
600	20	More new grains formed up to shear, 0.17

to give good correlations between the shape of the new crystal and the structure of the deformed matrix as follows:

When the crystal developed no bands and the deformation was small, as with A-4 and A-1, both the primary and conjugate slip planes seemed to affect the directional growth of the new crystals. If, however, the deformation was large with no band formation, only the primary slip plane seemed decisive (Fig. 4 from A-5). On the other hand, when bands were profusely developed, the shape of the new grain was defined by the bands (Fig. 5a from A-18). Nevertheless, when bands were at an early stage of formation, both primary slip plane and band appeared to influence the outline of the new grain. Since the band was perpendicular to the primary slip plane, the new grain thus possessed a rather flat boundary (Fig. 5b from A-1').

This structure-sensitive characteristic of nucleation and growth was also prominent among the three specimens, A-3, A-6, and A-2 which formed polycrystals upon annealing (Fig. 6a and b). In the case of A-2, this was even more pronounced, in that all of the grains have aligned themselves along deformation bands developed in the prior straining process, Fig. 7. By locating approximately the bands outlined by the grains it was found that these were the ones which formed initially at the early stages of deformation but had undergone further rotations, as discussed in the previous paper.

Recovery

Two specimens (A-13 and A-15) did not form new crystals after a treatment of 24 hr at 600 C. X-ray photograms showed that the Laue spots had undergone some minor changes indicating recovery or polygonization. A similar phenomenon was observed in crystal A-2 after the first extension and the first anneal.

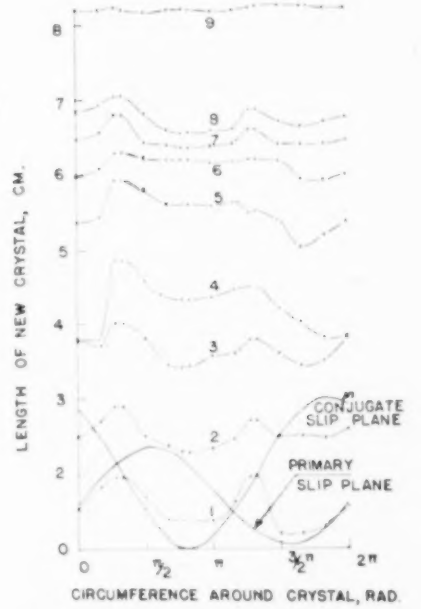

Fig. 3—Developed curves showing crystal growth in specimen A-4, with relation to primary and conjugate slip planes at nine intermittent anneals at 600 C.

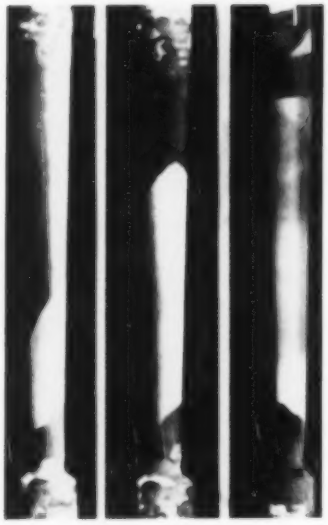

Fig. 4—Crystal growth in specimen A-5. The shape of the growing front of the new crystal follows very closely the glide ellipses from primary slip. X1.

Although crystals A-17, A-20, and A-18 recrystallized with the formation of a single grain in each case, the new grain did not grow to the large end of the taper where the strain was still measurable, nor did additional grains form even after a prolonged anneal of 24 hr at 600 C. Again, the matrix which had been annealed but did not recrystallize, exhibited only minor alteration of the Laue spots; i.e., polygonization.

There was a factor common to the crystals described above which should be emphasized, viz., they all developed deformation bands during the straining process. On the other hand, in crystals A-1, A-4, and A-16 which revealed no band formation, the new crystal grew to the low strain end after isothermal annealing, for periods less than 7 hr at 600 C. In the case of A-3 (no band formation), subjected to cumulative treatment, recrystallization proceeded as if recovery had exerted no effect. Thus, it seemed highly probable that the structural condition associated with band formation was more susceptible to polygonization or recovery than the structural condition of other crystals with no band formation.

Orientational Relationships

In most cases a simple relationship could not be found between the orientations of the new crystals and the matrix. Thus, great difficulty was experienced in any attempt to correlate these orientations from a point of view that the new grains were not randomly produced in the strained matrix. For a tentative analysis, the data on orientational relationships between the seven new single crystals and their matrices are presented according to the scheme used earlier by Mathewson[3] (Figs. 8 to 14). This scheme consists in locating an axis of rotation in an original {111} plane (whose pole is closest to one of the octahedral poles of the recrystallized grains) which would transfer this plane to its new location, and then adjusting the positions of all other rotated poles to their observed final positions by a second rotation, this time around the pole of the relocated {111} plane. Table III summarizes the data from these seven crystals together with data derived from the investigations reported by Carpenter and Elam[2] and Collins and Mathewson.[4] The basis for the above procedure has been suggested earlier in this paper and is further defined as follows:

First of all, it is noticed that in no case, Table III, was the fourth octahedral pole of the parent crystal observed to be the octahedral pole closest to a similar pole of the new crystal, i.e., most likely to represent the same plane somewhat displaced by plastic action. It is the slip plane corresponding to this pole that was never found operative in the authors' studies of plastic deformation. This agrees with the general deduction that if displaced remnants of {111} glide packets in the slipped matrix, strained into contact with similar fragments, are the regions of preformation of recrystallization nuclei, then an orientational association with the observed operative slip planes (primary, conjugate, and cross-slip planes) would be expected. Second, the rotation about the axis A in each case seems to represent an average value not greatly different from either 22° or 38°, except in the two cases of A-18 and A-20. This type of rotation of 22° or 38° about a <111> axis is similar to that required by Kronberg and Wilson[1] in their interpretation of oriented nucleus formation. Its significance lies in the observation that lattice readjustments could take place by small movements of the atoms around coincidence sites in the stacking of octahedral planes. It is held that the strain which might account for these small atomic movements is derived from the twisting of the glide lamellae in the vicinity of slip sites during the operation of a process of congruent-incongruent shear in the plastic extension of the crystal.[3]

In such cases as A-18 and A-20, which would seem to require a second rotation of approximately 60°, a simpler orientational relationship could be rationalized by twinning, as previously described by Mathewson[3] with relation to certain brass crystals. A stereographic plot of crystal A-20 from this point of view is shown in Fig. 15.

Among the specimens which formed polycrystals,

Table III. Orientation Relationship Between a New Single Crystal and Its Matrix

Crystal	Nearest Octahedral Pole of the Parent Crystal	Strain Rotation About A (Degrees)	Second Rotation About A (Degrees)	Deviation of the Second Rotation from 22° or 38°	Remarks
A-1	Conjugate S. P.	9	17	5	
A-3	Primary S. P.	25	22	0	
A-4	Conjugate S. P.	7	33	5	
A-5	Conjugate S. P.	26	35	3	
A-16	Primary S. P.	7	42	4	
A-18	Conjugate S. P.	17	58	2	Can be resolved by twinning
A-20	Primary S. P.	14	60	1	
No. 78	Conjugate S. P.	13	34	3	Data reinterpreted from Carpenter and Elam[2]
No. 79	Cross S. P.	17	15	1	
No. 86	Cross S. P.	19	41	3	
No. 88	Conjugate S. P.	13	59	2	
B-2	Cross S. P.	20	37	1	Data reinterpreted from Collins and Mathewson[4]
B-3	Conjugate S. P.	10	52	7	Can be resolved by twinning

a b

Fig. 5a—Crystal growth in specimen A-18. The shape of the new crystal is parallel to the original deformation bands. X1.

Fig. 5b—Crystal growth in specimen A-1. The shape of the new crystal is flat around the circumference. Note the unrecrystallized matrix A-1 still shows the faint set of deformation bands in the middle section. The darkest shade near the large end represents the mother crystal A-1, from which the single crystal A-1 was obtained by annealing at 600° for 2 hr. X1.

again used in analyzing 18 of these grains. The first rotation varied from 5° to 25°, while the second rotation amounted to either 22° or 38° (±3°) in nine grains and varied from 30° to 55° in the others. Again, no pole representing so-called "forbidden" slip in the matrix came closest to an octahedral pole of the new crystals.

Discussion of Results

It is noteworthy that the amount of strain in a tapered aluminum crystal can vary within wide limits, e.g., from 1.2 to 54.4 pct elongation, and still yield a recrystallized single crystal by subsequent annealing at 600°C. It seems that the magnitude of the taper (slope, 0.053) giving rise to the "strain gradient" and the temperature of anneal (600°C) have constituted "critical" combined factors favoring crystal growth. Burke and Shiau[1] have shown that when a region of fine-grained structure is swept by a moving grain boundary, the specimen loses its capacity to form recrystallization nuclei. Thus, nucleation and growth are competitive processes and in the present case, if sufficient growth of one nucleus at the higher stressed end of the crystal occurs during the incubation period for nucleation, other recrystallization nuclei do not appear.

Fig. 6a—Crystal A-3. Grain formation in slip bands. X12.

Fig. 6b—Crystal A-2. Nucleus formation in deformation bands. X12. Area reduced approximately 30 pct in reproduction.

A-2 as well as A-6 produced a highly preferred orientation at the small end of the taper (cf. Fig. 7), while in the remaining parts of the crystal, the orientations of the new grains were rather widely spread. The data are plotted in standard projections in Fig. 16a to e, which represent, respectively, the orientations of grains in five different average positions on the tapered crystal. It is readily seen from Fig. 16a that the orientations of the 25 new grains in this section can be rather closely derived by a simple rotation of 37° to 40° of their poles around the particular <111> pole which possessed approximately the same location as the cross-slip pole in the matrix. Fig. 16b represents the orientations of six fairly large grains at a larger section next to the grain clusters plotted in Fig. 16a. Here grains 2, 24, and 25 can be similarly related to the matrix as indicated above, while the other grains begin to show pronounced scattering. From this section onward, up to the large end of the crystal (Fig. 16c, d, and e), simple relations between matrix and new crystals apparently did not occur. However, a general survey showed that most of the grains plotted in Fig. 16c, d, and e gave the 22° to 38° relationship in an analysis by the dual rotational process. Some of them can be related by the mechanism of twinning, as previously described.

The orientations of the new grains formed in crystal A-3 during the cumulative annealing are widely scattered in all sections along the specimen. The dual-rotational scheme previously described was

Fig. 7—Two views of recrystallized grains outlined by deformation bands in crystal A-2. X1.

Fig. 8—Crystal A-1

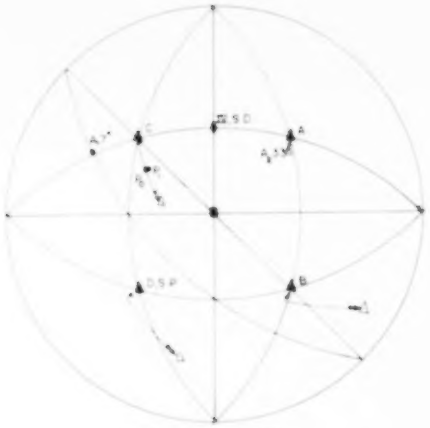

Fig. 10—Crystal A-4

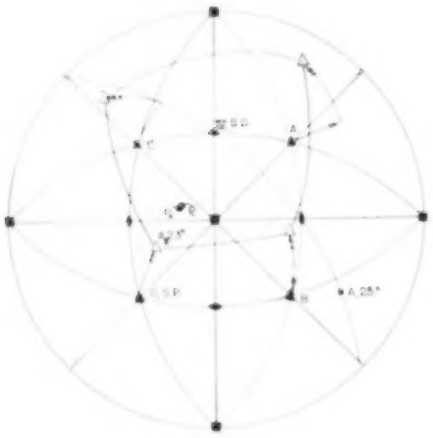

Fig. 9—Crystal A-1

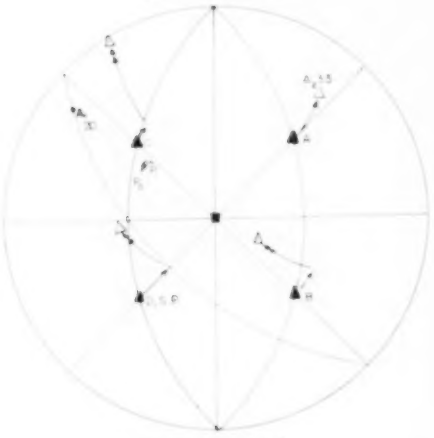

Fig. 11—Crystal A-5

Figs. 8 to 14—Stereographic projections showing constructions giving orientations of new aluminum single crystals (open triangles) from orientations of original strained crystals (black triangles). P, pole of stress axis; A_1, first axis of rotation; and A_2, second axis of rotation.

The study of the shape of the new grains has clarified various observations made by other investigators. Thus, Karnop and Sachs[7] reported that the inner face of crystal growth in aluminum was parallel to the old glide plane, whereas Collins and Mathewson[8] observed that it was parallel to the plane of the deformation band. The present results confirmed both observations and gave direct evidence that these features of growth are greatly influenced by the structure of the deformed lattice. However, the effect of surface energy on the shape of the new crystal is also apparent, as indicated by the decreasing curvature of the crystal boundary during growth, cf. Figs. 1 and 4.

The growth features shown in Fig. 2 are different in two respects from those associated with ordinary growth rate curves, i.e., 1—since the crystal is tapered, the amount of the matrix to be consumed by the growing nucleus varies along the crystal, and 2—the strain in the matrix also varies along the specimen. It can be seen, however, from Fig. 2 that, in general, the rate of crystal growth is greater in specimens subjected to the greater strain. Compare especially specimens A-16, A-5, A-1, and A-4, where A-16 was strained to 29.5 pct at the small end of the crystal and A-4 only 1.22 pct, with A-1 and A-5 at intermediate positions. With crystals A-20, A-18, and A-1' which developed deformation bands, the effect of recovery seems noticeably to have influenced the observed growth phenomena. Here, the new crystals stopped growing at an intermediate position in the matrix even after prolonged annealing. The long period of incubation of the severely deformed specimen, A-18, at the small end of the taper (elongation, 54.5 pct, with irregular bands) together with the small capacity of the new crystal to grow is remarkable. This is comparable, however, to the observation by Anderson and Mehl[9] that the rate of growth in specimens elongated as much as 90 pct was essentially the same as in specimens strained 15 pct.

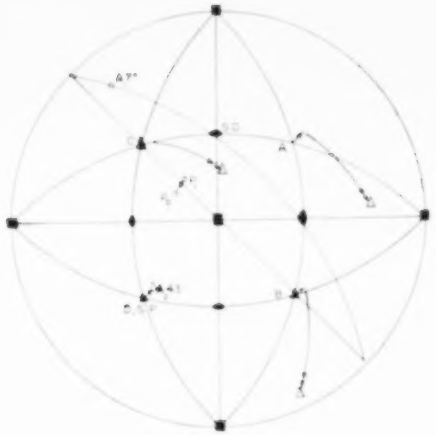

Fig. 12—Crystal A 16.

Fig. 14—Crystal A 20.

Fig. 13—Crystal A 18.

The exact mechanism of recovery is not understood. Burgers[7] has considered the process in terms of the solution and neutralization of dislocations, whereas others have considered recovery in terms of polygonization. In the present experiments, crystals with deformation bands were more susceptible to recovery than crystals showing no band formation but comparable amounts of elongation. Thus the process of recovery seems to be more closely associated with the intimate strain configuration than with the net value of strain. Furthermore, since deformation bands are readily formed in aluminum during plastic deformation, the above observations on the recovery of aluminum single crystals confirm the general belief that aluminum recovers rather more easily than other face-centered cubic metals.

The orientations of new grains formed during subsequent annealing of an aluminum single crystal after slight to moderate extension cannot be related to their matrix by a simple rotation about <111> or any other single axis in the crystal. The general method adopted by Mathewson[5] for relating the orientation of the new grains to that of the original crystal by a process of dual rotations has therefore been further tested. It has been demonstrated that first of all the "forbidden" slip pole was never found closest to an octahedral pole of the new crystal. This is in harmony with certain general deductions which have been made concerning the interrelationships between deformation and recrystallization. Secondly, a somewhat restricted value of rotation was required for the second operation (approximating either 38° or 22°) and this presents strong evidence in favor of the Kronberg and Wilson mechanism.[8] These two observations of selective action indicate that the numerous orientations that may come from a single deformed crystal are not wholly random, but are direct consequences of the oriented deformation process and of oriented nucleation.

In seeking the origin of oriented nuclei in the

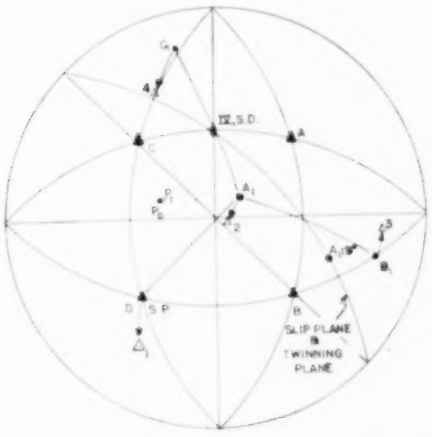

Fig. 15—Crystal A 20. Stereographic projection with constructions showing twin relationship between old and new crystals. Original octahedral poles shown as black triangles. An orientation twinned about D shown by filled circles. Octahedral poles of new crystal shown as open triangles.

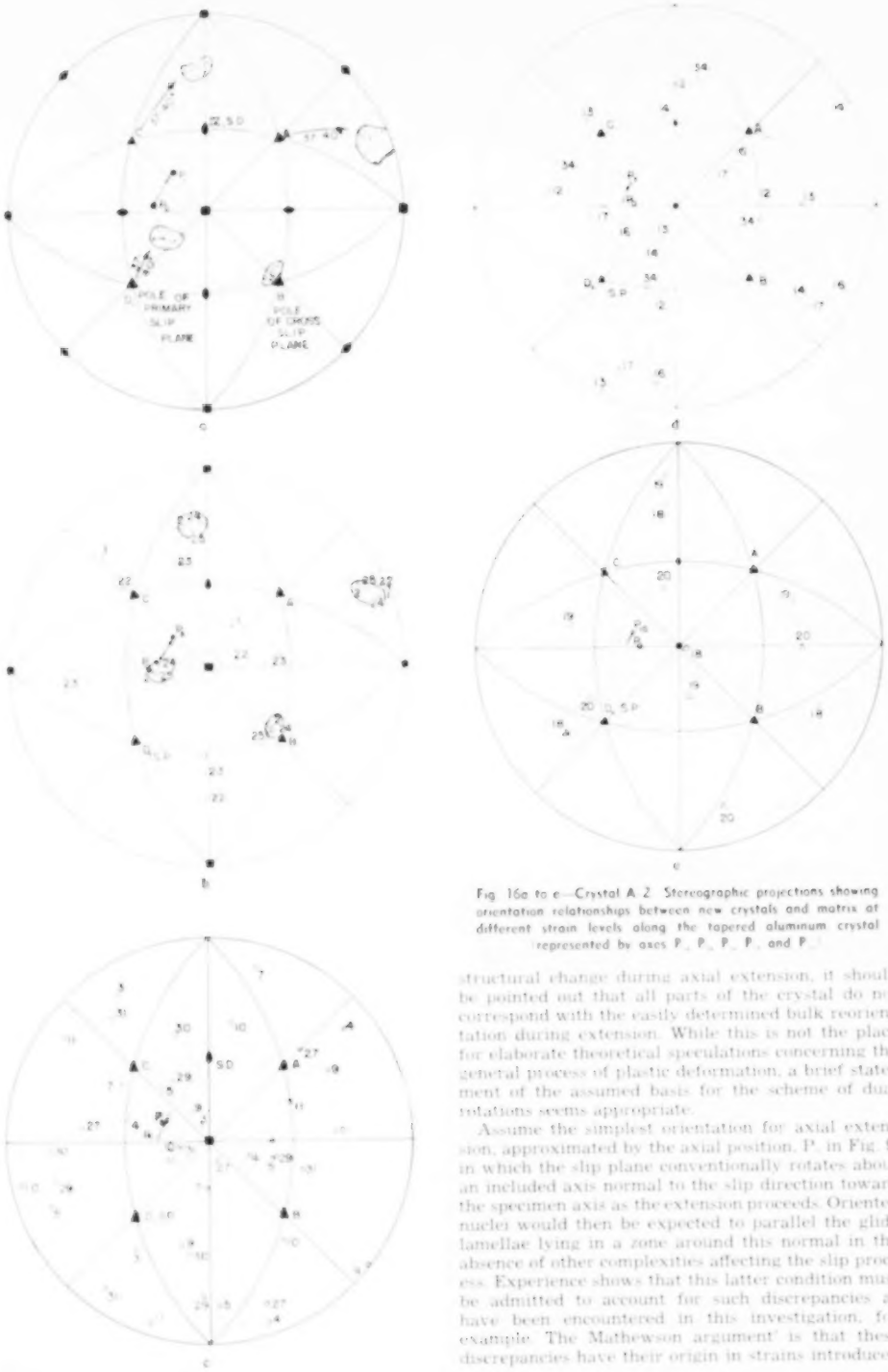

Fig. 16a to e—Crystal A 2. Stereographic projections showing orientation relationships between new crystals and matrix at different strain levels along the tapered aluminum crystal represented by axes P_a, P_b, P_c, P_d, and P_e.

structural change during axial extension, it should be pointed out that all parts of the crystal do not correspond with the easily determined bulk reorientation during extension. While this is not the place for elaborate theoretical speculations concerning the general process of plastic deformation, a brief statement of the assumed basis for the scheme of dual rotations seems appropriate.

Assume the simplest orientation for axial extension, approximated by the axial position, P, in Fig. 9, in which the slip plane conventionally rotates about an included axis normal to the slip direction toward the specimen axis as the extension proceeds. Oriented nuclei would then be expected to parallel the glide lamellae lying in a zone around this normal in the absence of other complexities affecting the slip process. Experience shows that this latter condition must be admitted to account for such discrepancies as have been encountered in this investigation, for example. The Mathewson argument[1] is that these discrepancies have their origin in strains introduced

by slip which theoretically is forced to assume <112> directions at the boundaries between glide lamellae, while the principal substance of the lamellae is displaced in the conventional <110> direction in response to a critical shear stress along <110> fibers of the crystal. The shear is thus congruent with the inner driving force in part of a glide lamella but incongruent at the slip site, and indeed it may be argued that incapability of the displacement to take place everywhere in line with the inner application of the force is responsible for the break-up into lamellae.

There are thus two different elements of slip and rotation operating side by side in the glide lamellae as extension proceeds, and this is held to account for the torsional disturbance around {111} slip poles actually observed in the experiments reported by Mathewson. Clearly in such a situation the sites for oriented recrystallization nuclei would be found in zones around axes deviating from the standard <112> axis of rotation, i.e., rotation about a variable axis in the slip plane, and a quantitative estimate of this deviation would call for knowledge of the precise pattern of strain at the slip sites. The authors, therefore, rationalize the reoriented grains by a first rotation around a variable axis in the slip plane followed by a second rotation around the pole of the relocated slip plane, attributed to the torsional disturbance as a factor in initiating changes allied to the Kronberg and Wilson mechanism. The final result is of course a wide spread of orientations among the recrystallized grains approximating the random condition.

It would be satisfying to find an explanation for the distribution of the common poles of the new grains around the cross-slip pole in the heavily deformed crystals A-2 (cf. Fig. 16) and A-6 and their rather unique clockwise rotation of 37° to 40° about this pole. The bulk rotation, P'-P, of 23° is around an axis close to the cross-slip pole and would, of course, move the original octahedral poles (filled triangles) 23° in the opposite sense to the indicated axial change. Thus the 37° to 40° clockwise rotation, previously noted, added to the 23° counterclockwise rotation, defining the general orientation of the strained matrix, shows a twin relationship between the new crystals and this strained matrix, i.e., 60° rotation around the pole of the twinning plane where the grains have presumably nucleated. There is, of course, the probability that the Kronberg and Wilson mechanism has been operative here. Whatever the details of the process involved, there is good reason to believe that strains residing in the lattice after deformation can be dissipated by reorientations having distinct crystallographic significance in relation to these strains.

Conclusions

1—The shapes of new crystals were carefully studied in relation to the structure of the strained matrix. In the absence of band formation the inner face of crystal growth lies parallel to the old glide plane; whereas, with band formation, the inner face is decisively affected by the band. Cooperative influence, involving the conjugate slip plane, in addition to the primary plane and the deformation band, was also observed.

2—Crystals with deformation bands were found more susceptible to recovery or "polygonization" than other crystals. Since deformation bands are readily formed in aluminum during plastic deformation, this observation may also be interpreted to explain the fact that aluminum recovers from residual plastic strain with greater facility than most face-centered cubic metals.

3—A unique phenomenon, viz., the growth of a single nucleus from a previously tapered and strained single crystalline matrix was observed over a wide range of pre-existing strain. The results seem to indicate that the magnitude of the taper and the (600 C) annealing temperature have constituted critical combined factors favorable to growth.

4—The orientations of new grains formed during subsequent annealing of an aluminum single crystal after slight to moderate extension can be related to their matrix by a double rotation based upon a theoretical interpretation of the slip process. In two cases representing heavily deformed specimens, a highly preferred orientation of the new grains was found, and its twinned relationship to the matrix could be rather closely derived by a simple rotation of <111> poles around the pole of the cross-slip plane in the matrix.

Acknowledgment

The authors wish to thank W. R. Hibbard, Jr. for his interest and help concerning this work, and to acknowledge their gratitude to M. L. Kronberg and R. Maddin for helpful discussions.

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Chromium-Nickel Phase Diagram (paper by D. S. Bloom and N. J. Grant. JOURNAL OF METALS, November 1951, p. 1089) 523

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Role of Gases in the Production of High Density Powder Compacts (paper by D. Warren and J. F. Libsch. JOURNAL OF METALS, September 1951, p. 774) 540

* TP 3305E

Powder Metallurgy of Zirconium

DISCUSSION, L. A. Bowen and Robert Steinitz presiding

A. Blainey (*Ministry of Supply, Atomic Energy Research Establishment, Harwell, England*)—With reference to the published work of Hausner et al. on the powder metallurgy of zirconium, it will be of interest to summarize briefly the results of preliminary work we have carried out on this subject at A.E.R.E., Harwell. For the early experiments we used zirconium

and zirconium hydride powders supplied by Metal Hydrides Inc. Vacuum sintering of powder compacts, cold formed at pressures up to 35 tons per sq in., was performed in Nimonic alloy tubes heated externally. The zirconium powder compacts were placed in recrystallized alumina boats and sintered in vacuo (10^{-5} mm Hg) at 1100°C. Graphite boats were not used, since work on the sintering of other reactive metal powders in such containers had indicated that reaction with the adsorbed gases occurs during sintering. Since the zirconium powder used in these experiments contained several percentages of oxygen, the sintered compacts were brittle, having a hardness of 400 to 500 Vickers, density up to 6.36 g per cu cm, and a transverse rupture strength of up to 19 tons per sq in. A compact containing 2 pct ZrH_2 sintered under the same conditions showed an increase in density and reduction in hardness (both slight) and a considerable (33 pct) increase in rupture strength. This work is being continued and extended at Liverpool University.

Hot compacting of these powders in protective atmospheres in cermet dies heated by radiation was also investigated. A pressure of 17.5 tons per sq in. was used at temperatures of 500° to 850°C. The ZrH_2 compacts disintegrated a short time after ejection from the die, presumably due to internal stress caused by the hydrogen remaining in solid solution. Strong compacts with a density up to 6.45 g per cu cm and rupture strength up to 37 tons per sq in. were formed from the zirconium powder under these conditions.

The following comparisons may be made between the work of Hausner et al. and our own. We use heated magnesium turnings, found to be more effective than uranium, to remove traces of nitrogen and oxygen from sintering atmospheres. It is necessary to purge the system very thoroughly, by repeated evacuation, to remove traces of air, and a high rate of argon flow is necessary in temperature ranges where considerable outgassing of the furnace tube occurs. Our experience with the sintering of beryllium compacts in alumina shows that appreciable quantities of aluminum are picked up by the beryllium, no doubt by a mechanism similar to that responsible for the pickup of beryllium by zirconium sintered in beryllia.

H. H. Hausner (authors' reply)—The low density and brittleness of the cold compacted and vacuum sintered zirconium was probably due to the relative impurity of the raw material and to the low temperature at which the compact was sintered. Mr. Blainey did not mention the sintering time, which plays an important role, especially at low sintering temperatures.

Zirconium hydride powder can be hot compacted when the process occurs in vacuum and at a temperature above 800°C. This fairly high pressing temperature is necessary for the decomposition but makes hot pressing of the hydride very unattractive. Hot pressing of zirconium powder, however, offers some advantages. It can be done at a temperature as low as 600°C and sinters by application of the necessary pressure to the full density. The compacting pressure depends on the size of the compact and on the type of lubrication. According to my own experience, hot pressed zirconium is considerably less ductile than when cold compacted and vacuum sintered.

Y. C. Chuang and **S. J. Kennett** (*Dept. of Metallurgy, The University, Liverpool, England*)—We were particularly interested in this paper as similar work is in progress here. Most of our experiments have been carried out starting with turnings prepared from magnesium-reduced zirconium (containing 0.08 pct Fe and 0.13 pct C). The turnings are converted to hydride by heating in hydrogen at 600°C for 1 hr (the hydrogen having been passed over copper at 800°C and magnesium turnings at 600°C).

In order to reduce oxygen pickup during pulverizing, the hydride is shaken in an alloy steel tube, together with steel balls (½ and ¼ in. in diam), the tube being closed with rubber bungs and kept filled with nitrogen. The powder is then mechanically screened by shaking on 100 and 200 mesh sieves, successively. After shaking for 5 hr the −100 mesh product contains about 50 pct −200 mesh material. The original oxygen content of the zirconium is 0.026 pct and that of the −100 to +200 and of the −200 mesh hydride 0.05 and 0.04 pct respectively. Iron pickup is small, 0.09 pct in the powder compared with 0.08 pct in the original metal.

We confirm that the hydride sinters much more readily than zirconium powder. The −200 mesh material gives a sintered compact of lower transverse rupture strength, possibly due to a concentration of carbide in the finer of the particles produced by pulverizing. Further experiments are now being made with a purer form of zirconium containing only 0.02 pct C. Fuller details of our work will be published later.

H. H. Hausner—I think that pulverizing the hydride in nitrogen may permit picking up nitrogen during the ball-mill treatment. The presence of nitrogen has many disadvantages, especially with regard to the corrosion resistance of the material.

Grain Structure of Aluminum-Killed, Low Carbon Steel Sheets

DISCUSSION, B. L. Averbach presiding

P. A. Beck (*College of Engineering, University of Illinois, Urbana, Ill.*)—This investigation offers some good evidence in favor of the aluminum nitride explanation of grain-growth inhibition in aluminum-killed steels. It is particularly interesting that the coarsening temperature of such steels was found to be associated with greatly increasing solubility of aluminum nitride. This conclusion of the authors is in excellent agreement with our own results on coarsening in Al-Mn alloys.[1]

In these alloys, where the inhibiting particles can be directly observed under the microscope, it was found that abrupt coarsening takes place when specimens containing the Al-Mn compound in fine dispersion are heated to a temperature just below the solvus point for the particular composition. The largest grains can be obtained at a temperature, where a small residual amount of precipitate was still present. When temperatures about 10°C above the solvus point were used and the precipitate was completely redissolved, normal gradual grain growth took place and, because

[1] P. A. Beck, M. L. Holzworth, and P. R. Sperry: Effect of a Dispersed Phase on Grain Growth in Al-Mn Alloys, *Trans.* AIME (1949) **180**, p. 163; METALS TECHNOLOGY (September 1948).

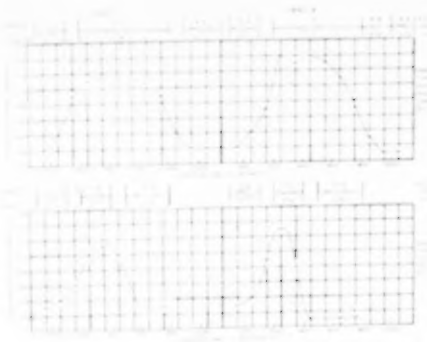

Fig. 11—Influence of aluminum nitride on ferrite grains.

of the specimen thickness limitation, the resulting grain size was considerably smaller than at a somewhat lower annealing temperature.

A further strategy in support of the authors' conclusion that second-phase inhibition is responsible for the refinement of elongated grain shapes in cold rolled and annealed steels is offered by the experience that such grain shapes occur in cold rolled and annealed commercial aluminum alloys containing finely dispersed inhibiting particles.

H. T. Clark (*Jones and Laughlin Steel Corp., Pittsburgh*)—It is gratifying to know that the methods for the determination of nitrogen and aluminum nitride have been useful to others as well as ourselves.

After the development of the method for determining aluminum nitride, work similar to that discussed in this paper was also carried on at Jones and Laughlin. In general, our data support the conclusions reached by the authors, but there are several aspects of this whole problem that remain quite puzzling.

We have made continued efforts to obtain microscopic evidence of aluminum nitride particles in steel but have not been able to satisfy ourselves that we have observed this compound. Without such evidence, it is difficult to establish precisely how aluminum nitride influences grain shape and size, or how it controls such properties as strain-aging behavior.

It is also difficult to explain why the aluminum nitride recovery is low for steels rapidly cooled from very high temperatures. Beeghly's method provides analytical evidence that the compound is profoundly changed at these temperatures but cannot provide an answer regarding the condition of the aluminum nitride. It still may be present in the steel after such heat treatment, but not retained on the filter, or it may no longer exist as a compound.

Soon after the development of the analytical method, it was determined that the amount of aluminum nitride present in cold rolled, annealed, aluminum-killed strip steel could not be related to the microstructure, equiaxed and elongated grain material were found to have similar aluminum nitride contents. This stimulated further investigation of the problem, and it is believed that some of the results obtained, showing the difference in formation of aluminum nitride on cooling as compared to heating and the effect on grain shape, constitute a pertinent addition to the present paper.

To determine the influence of aluminum nitride on the formation of equiaxed or elongated ferrite grains during subcritical annealing, hot band samples from two heats were treated in a temperature-gradient furnace similar to the one described by Halley.[7] Two series of specimens were used, one was preheated for 15 min at 2250 F before being placed in the gradient furnace, and the other was heated from room temperature. Both were held for 1 hr in the gradient furnace at temperatures between 900 and 2100 F followed by air cooling. Part of each series was sectioned for aluminum nitride determinations, part was cold rolled 45 pct and another part 50 pct, after which they were annealed at 1300 F and examined metallographically.

The results are summarized in Fig. 11. The curves of aluminum nitride vs. heating temperature follow the same general trend shown in Fig. 8 of the paper although the breadth of the high AlN plateau is not the same for the two heats. However, the curves obtained on cooling are somewhat different. Retarded cooling did not result in an increase in aluminum nitride until temperatures below 1600 F were reached. In both heats, a maximum value was obtained in a fairly narrow range near 1300 F. Arrested cooling at lower temperatures resulted in progressively lower amounts of aluminum nitride.

The microstructures obtained after cold rolling and annealing are described above each curve. The only effect of the amount of cold reduction in this experiment was a slightly finer grain size in most cases, for the samples cold rolled 50 pct as compared with those reduced 45 pct. All samples containing more than about 0.005 pct AlN (corresponding to about 0.0016 pct N as AlN) before cold rolling produced equiaxed or mixed ferrite grain structures during annealing. All annealed samples had high AlN contents regardless of the prior treatment.

To obtain elongated ferrite grains after annealing, the aluminum nitride content must be low before cold rolling and high after annealing. It is necessary to rapidly cool hot rolled, aluminum-killed strip to below 1200 F for the desired elongated grain structure in the finished material.

From these and the authors' data, it seems that the formation (or precipitation) of aluminum nitride during annealing is a basic condition to the production of "satisfactory," aluminum-killed, deep drawing strip steel. However, a sufficient number of exceptions have arisen to indicate that other factors may also be important in controlling grain shape. It seems fitting to call attention to some of these.

1—The data presented in Table VIII of the paper point to the soluble aluminum content as an important factor. Samples 2D and 2E, with more than 0.066 pct Al, had intermediate or equiaxed grains, even though apparently a sufficient amount of AlN to produce elongated grains was precipitated during annealing.

2—Finally, we would like to call attention to the apparent influence of carbon content on grain shape. With normal mill practice, elongated grains are obtained except when the carbon content is 0.05 pct or over. In these cases, equiaxed grains result regardless of the aluminum and nitrogen contents of the steel.

As yet, we have no satisfactory explanation for these apparent anomalies and would be interested in the comments of the authors.

R. L. Solter and **C. W. Beattie** (authors' reply)—The discussions presented by Dr. Beck and Mr. Clark by analogy and by additional data tend to support the authors' conclusions as to the behavior of aluminum nitride in aluminum-killed, low carbon steel sheets. It is unfortunate that we have been unable to observe the inhibiting particles directly by microscope as was possible for the Al-Mn alloys studied by Dr. Beck.

The curves shown in Fig. 11 of Mr. Clark's discussion further emphasize that a detailed knowledge of prior treatment is required for a complete understanding of the behavior of aluminum nitride. As stated by Mr. Clark, additional factors may also be important in controlling grain shape. We did not have sufficient data to establish a definite limiting value for the nitrogen precipitated as aluminum nitride required to produce the elongated grain shape. However, as shown by values for 2C, 2D, and 2E in Table VIII, 0.0031 pct precipitated caused an elongated grain

structure, 0.0023 pct an intermediate, and 0.0021 pct a rounded grain structure. Mr. Clark's observation that all samples in his experiments with more than 0.0016 pct produced equiaxed or mixed ferrite grain structures is not incompatible, when it is considered: 1—that samples 2C, 2D, and 2E contained differing amounts of residual aluminum; and 2—that there may be differences in analytical results between laboratories.

We did not use steels with carbon contents as high as 0.06 pct in this investigation, but in other experiments have produced elongated grains in steels containing as much as 0.25 pct C. Consequently, we can only suggest that Mr. Clark's experience with higher carbon content may be associated with a different degree of response of these steels to his normal mill practice.

Theory of Grain Boundary Migration Rates

DISCUSSION, B. L. Averbach presiding

Lo-ching Chang (*School of Mines, Columbia University, New York*)—The paper is an excellent example of how fundamental information can be obtained through careful analysis and thoughtful interpretation of published data.

Regarding the local melting hypothesis for grain boundary flow appearing in the latter part of the paper, the author will perhaps recall Barrer's theoretical treatment[1] of the viscosity of pure liquid metals. According to his "zone" theory of viscous flow and diffusion, the energy of activation, E_v, is not localized but is distributed over a zone of degrees of freedom within the liquid. The absorption of E_v loosens the liquid in this zone as a prerequisite for viscous flow or diffusion. The size of the activated zone is measured by the number of degrees of freedom, f, contained in it, and calculation shows that f varies between 1 to 3 for liquid metals. This seems to indicate that diffusion or viscous flow in liquid metals has a relatively simple mechanism. If in viscous flow the activated zone is limited to only 1 to 3 degrees of freedom, is it necessary to loosen by melting from 10 to 34 atoms for grain boundary migration to take place, which would involve an activated zone containing 10 to 34 degrees of freedom, about an order of magnitude larger than that predicted for viscous flow?

Second, does not the correspondence between Q and Q_v (see Table I of the paper), both of which seem to correlate rather well with the sublimation energy of the metal,[2] suggest that the fundamental mechanism for self-diffusion and for grain boundary diffusion in a metal is probably the same? The vacancy mechanism of diffusion, for instance, requires that the diffusion rate be proportional to the number of vacancies in the metal participating in the diffusion act. Modern theories of the grain boundary model predict a higher density of dislocations, which act as sources and sinks for vacancies, near a grain boundary than inside the volume of the grain. Does not the vacancy mechanism of diffusion also predict relatively large mobility at a grain boundary?

It is our belief that a real knowledge of the mechanism of diffusion plus further experimental work on grain boundary mobility as may be affected by orientation difference, concentration of impurities, state of strain, etc., will lead to a far-reaching understanding of the grain boundary phenomena.

C. S. Smith (*Institute for the Study of Metals, University of Chicago, Chicago*)—Though I agree with Dr. Turnbull regarding the mathematics involved, I believe his insistence on the phrase "nucleation and growth" for the recrystallization process is unfortunate. Though the possibility of fluctuations, which give rise to crystals of quite different orientation despite the high interface energy involved, cannot be ruled out entirely, it seems much more likely that the phenomenon of recrystallization is one of movement of interfaces already present. It may be true that all of the mysterious things occurring before a given grain gets so large that it can advance at a linear rate into its neighbors follow the same mathematics as a nucleation process; however, the term nucleation has by many years of common usage become associated with the formation (by thermal fluctuation or otherwise) of a discrete volume of a new phase that did not exist before, separated from the old material of the matrix phase by an interface whose free energy must somehow be provided and which is generally the controlling factor in the process. If no new interfaces need form in recrystallization, surely the term nucleation is an undesirable one.

R. R. Hasiguti (*Dept. of Metallurgy, Faculty of Engineering, University of Tokyo, Tokyo, Japan*)—I am very glad to know that the author has found the unexpectedly large entropy of activation in boundary migration processes in various kinds of materials, because it agrees completely with my paper,[3] which was presented at the fall meeting of Jananese Institute of Metals in 1948. In that paper I suggested that the length of the unit of elementary process measured parallel to the direction of boundary migration should be far larger than the atomic spacing to account for the apparently large entropy of activation. By the unit of elementary process, I mean an atom or a group of atoms which goes from its initial to final state across a potential barrier by just one activation. This unit might be interpreted as a group of atoms which melt at the advancing boundary, as Mott suggests, but I am rather inclined to consider that the crystal remains solid without melting. If we assume the dislocation model of grain boundary, the boundary migration may be interpreted as due to the travel of dislocations, which form the grain boundary, through the crystal which is to be swept by the migrating boundary. Then it may be natural to consider that the traveling distance of the once activated dislocations is far larger than the atomic spacing. This traveling distance of dislocations corresponds to the length of the unit of elementary process.

If the above picture is true, we may further consider that the traveling distance of dislocations, or the length of the unit of the elementary process, will increase when the temperature is raised. I have assumed that the length of the unit of the elementary process changes as a function of temperature according to the following equation:

$$l = l_0 \exp [-E_l/RT] \qquad [19]$$

where l is the length of the unit measured parallel to the direction of boundary migration; l_0 and E_l are constants; and R and T are the gas constant and the

[1] R. M. Barrer: Trans. Faraday Soc., (1941), 39, pp. 48 and 59.

[2] B. Chalmers: Progress in Metal Physics (1949), 1, p. 374.

[3] R. R. Hasiguti: Journal Physical Soc., Japan (1950), 5, p. 14. Errata of this paper are in the same Journal (1951), 6, p. 416.

absolute temperature, respectively. And then I have derived an equation for the rate of boundary migration G in the case of recrystallization as follows:

$$G = (a/\lambda)E_v/(RT)\exp[-(E+E_v)/RT] \quad [20]$$

where E is the activation energy of boundary migration in the absence of internal strain, τ, the time of relaxation for the movement of a group of atoms, E_v, the energy absorbed during cold working, and a, a constant which may be nearly equal to unity. $(E+E_v)$ corresponds to the experimental activation energy.

As the driving free energy ΔF of the present paper is nearly equal to E_v in eq 20, the following correspondence between the author's quantities and our quantities may be roughly established:

$$(1/kT)\exp[(\Delta S_v)_v/R] = 1/\tau \quad [21]$$

As kT/h is equal to the time of relaxation of atomic vibration τ_v, eq 21 can be written as

$$\exp[(\Delta S_v)_v/R] = (1/2\lambda)(\tau_v/\tau) \quad [22]$$

In order to obtain reasonable values of λ from eq 19, λ should be about 10^{-7} cm, which is about 10^{15} times larger than τ_v. If τ/τ_v is about 10^{7}, $(\Delta S_v)_v$ will be about 35 cal per mol per degree, which is in the range of entropies of activation tabulated in Table I of the paper. So in my opinion, the apparent large value of entropy of activation comes from the large value of λ in my equation. It is not easy, however, to find the physical meaning of λ, although mathematically it is the value of λ when the temperature becomes infinite. But I should like to emphasize that the physical meaning of λ is very clear, if we use the above-mentioned dislocation model of boundary migration.

The author tried, fairly successfully, to account for the large value of entropy of activation using Mott's fusion theory and Zener's inclusion theory. But I shall be very glad if he will try another possibility of explaining it, which I have mentioned here.

The author assumed that G is independent of time, if the temperature is kept constant. This is true in most cases. But in our laboratory we found recently that in the case of single crystals of aluminum the linear rate of growth of recrystallized grain decreases after a certain period of heating. Sometimes it was found that the grain stops growing completely. Of course the impingement of the recrystallized grain was avoided using conditions where one or two grains grow in the matrix of the strained single crystal. This result may be interpreted as due to the recovery of the matrix, which is fairly fast in the case of single crystals.

D. Turnbull (author's reply)—Dr. Chang has focused attention on the basic problem that the number of atoms that apparently have to be activated in grain boundary migration seems to be far greater than for diffusion in solids and possibly liquids, if Barrer's mechanism is accepted.

I believe that there is no marked correspondence between Q_v and Q_d. I agree with Dr. Chang that self-diffusion at grain boundaries may take place by a vacancy mechanism. Also as he implies there may be a high concentration of vacancies already in the grain boundary. From these assumptions, it seems to follow that Q_v should exceed Q_d approximately by the energy required to make a gram atom of lattice vacancies.

In reply to Dr. Smith, I favor dissociating connotations of mechanism from terms used to designate physical phenomena. That is, I believe that it is desirable to call a phenomenon one thing and the mechanisms used to explain the phenomenon something different. Thus, it will not be necessary to devise a new nomenclature for the same physical content every time the prevailing opinion about the mechanism underlying it changes, which is quite often—particularly in recrystallization.

Unfortunately, the term "nucleation" has been used in the past to denote certain mechanisms as well as the phenomena that they are supposed to "explain." I believe that either we must reserve the term nucleation to denote the specific mechanism that Dr. Smith indicates or use it to denote an event having some well-defined physical description as was done in my paper. If we were to adopt the Smith definition of nucleation, we should have to invent some new term for what commonly has been called nucleation in many crystallization and condensation processes. For "nucleation" of crystals or liquid droplets in supersaturated solutions can and probably often does occur without the formation of new interfaces, i.e., from retained nuclei."

My dissociation of any connotation of mechanism from the term nucleation is not new.[7] Also Burgers[8] used the term in describing recrystallization, even though he seemed to favor the same mechanism as Dr. Smith.

I thank Professor Hasiguti for his comments and for calling my attention to his interesting paper. His formulation is similar to Mott's, excepting that he assumes, on the basis of Suzuki's experiments, that the free energy driving recrystallization, ΔF, varies as strain, ϵ, squared. (I assumed a linear relation between ΔF and ϵ). Dr. Hasiguti's formulation led him to the same problem that concerned Mott, Smoluchowski, and me, namely: (in terms of the formalism of my paper): the abnormally large entropy of activation $(\Delta S_v)_v$ for boundary migration.

The solution of the problem proposed by Dr. Hasiguti is interesting, but his model is not sufficiently developed to reduce the number of disposable parameters, as Mott's theory does, or to permit other quantitative predictions. Also, I question the applicability of the dislocation model to high energy moving boundaries. On the other hand, something like Dr. Hasiguti's theory, if further developed, might be useful for describing the motion of low energy boundaries.

Dr. Hasiguti assumes, as does Mott, that ΔF is independent of temperature. As pointed out in my paper, a large apparent value of $(\Delta S_v)_v$ would be found if ΔF increased with temperature. In the paper the only process cited that would cause ΔF to increase with temperature is the solution and coalescence of inclusions with increasing temperature. Since writing the paper, two other possible explanations for a large apparent value of $(\Delta S_v)_v$ have come to my attention:

1—Assume that the matrix grains and the growing grains contain subboundaries. Now suppose that the density of subboundaries, d, in the grains that grow decreases markedly with increasing temperature, due to substructure coarsening, while d for the matrix grains is little affected by temperature. It follows that ΔF will increase with increasing temperature.

2—R. L. Fullman (private communication) has suggested that as the positive adsorption of soluble impurities at grain boundaries decreases with increasing temperature: (a) the energies of the boundaries consumed will increase thus causing an increase in ΔF and, (b) positively adsorbed solute atoms decrease the mobility of the boundary. Therefore, as the temperature is raised two factors operate to increase the boundary mobility—thermal activation and a decreased density of positively adsorbed atoms at the boundary. The operation of the second factor will lead to an apparently large $(\Delta S_v)_v$.

As Dr. Hasiguti indicates G is not always independent of time. Müller occasionally observed cessation of growth prior to impingement in his studies of the recrystallization of deformed, rock salt single crystals. Ms coworkers (A. M. Turkalo and H. N. Treaftis) and I have also observed the phenomenon in the secondary recrystallization of cube texture copper. The phenomenon may be caused by processes of recovery or grain growth in the matrix which reduce ΔF, or possibly the boundary motion is retarded by further concentration of positively adsorbed solute on it as the matrix boundaries are consumed.

[7] D. Turnbull, *Journal of Chemical Physics* (1950) **18**, p. 198.
[8] W. A. Johnson and R. F. Mehl, *Trans.* AIME (1939) **135**, p. 416.
[8] W. G. Burgers, *Rontgen's and Metall Physik*, Vol. 3 (1941) Leipzig.

DISCUSSION, B. L. Averbach presiding

W. R. Hibbard, Jr. (*General Electric Co., Schenectady*)—It has been found[1] that if copper wire is drawn

[1] W. R. Hibbard, Jr.: Journal Inst. Metals, (August 1950) p. 581.

99.8 pct reduction in diameter or more, the (100) component of the deformation texture may essentially disappear. The author's wires were drawn only 95.8 pct reduction in diameter from hot rolled stock. The (100) component might be further enhanced by prior hot working. Additional cold working leading to the disappearance of the (100) component might alter the recrystallization texture, since it appears to play an important role. In Fig. 6, there is considerable spread from the (112) texture on the (002) ring with variable intensity. Could these results also be interpreted as a (210) component? Is there any effect due to etching the wires?

G. Bassi (*author's reply*)—The expression "deformation texture" in Fig. 1 was originally chosen to describe the status of the wire after drawing, without taking any stand on the question of whether the [100] component was due to recrystallization or not.

After the publication of Hibbard's paper[1] according to which the final cold drawing texture is [111] for face-centered cubic metals, further investigations have been carried out.

After drawing a wire rod from 9.5 to 2.5 mm, it was annealed for 6 hr at 450°C. The diffraction film showed a random orientation of the grains as indicated by Fig. 9. The wire was then drawn to 0.3 mm, samples also being taken at several intermediate sizes. Even after about 95 pct area reduction (wire diam, 0.54 mm), there was a noticeable sharpening in the intensity of the interference spots of both [111] and [100] (Figs. 10 and 11). This is in disagreement with the results of Hibbard,[1] who found that [100] disappeared with increas-

[1] W. R. Hibbard, Jr.: Trans. AIME (1949) 185, p. 598; JOURNAL OF METALS, September 1949.

ing reduction. The wire was drawn in continuous machines with a low speed and the dies were immersed in a cool lubricating solution, so the final temperature of the wire was less than 50°C. Furthermore the X-ray diagrams were taken within a few hours of the drawing. Therefore it is not probable that any recrystallization occurred during the drawing or storing of the wire at room temperature. All the samples, except one, were etched to 0.15 mm before X-raying, in order to prevent the disturbing influence of the surface layer of the wire. Due to the friction in the dies, this layer has a diffuse texture.

The spread of the interference spots on the (002) ring measured as accurately as possible on the film of Fig. 6 in the paper, gave the following values:

Theoretical	Measured
35° 16'	33°-47°
65° 54'	61°-67°

It is true that the intensity of the spots varies in a way that is difficult to explain, but it will be still more difficult to justify a [210] interpretation. There is no spot on the (111) ring at $\chi = 75° 02'$ and the faint darkening at $\chi = 90°$ on the (002) ring is probably due to rests from the primary recrystallized [100] texture, also seen in Fig. 5 of the paper. The etching of the samples to a diameter of 0.15 mm probably has no influence. A sample that was etched before the annealing at 400°C also gave a [112] texture.

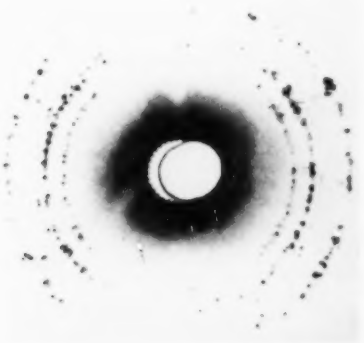

Fig. 9—X ray diagram of 2.5 mm wire after 6 hr at 450°C. Specimen etched to 0.35 mm and not rotated.

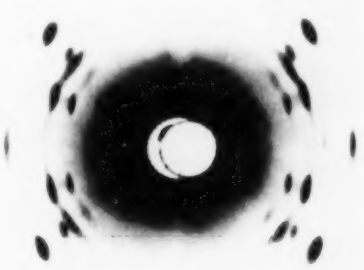

Fig. 10—Wire of Fig. 8 drawn to 0.54 mm. Etched to 0.14 mm. 95 pct reduction in area. (78.4 pct reduction in diam.)

Fig. 11—Wire of Fig. 8 drawn to 0.30 mm. Etched to 0.14 mm. 98.5 pct reduction in area. (88 pct reduction in diam.)

Systems Titanium-Molybdenum and Titanium-Columbium

DISCUSSION, M. Hansen presiding

P. K. Koh (*Research Laboratories, Allegheny Ludlum Steel Corp., Brackenridge, Pa.*)—One interesting deduction from the contribution by the authors could be that molybdenum or columbium plays the role of nickel or steels. One would wonder about the gross effect on the titanium matrix due to the alloying of molybdenum or columbium in the following respects. 1—How is the ductility of a titanium alloy improved by the addition of molybdenum or columbium? 2—What is the effect on the solid solubility of impurities in the titanium matrix through the alloying of molybdenum or columbium, especially regarding the contamination of oxygen and/or nitrogen?

The authors mentioned the existence of extraneous low angle lines in the Debye diffraction patterns on powder specimens of Ti-Mo and Ti-Cb alloys. These lines were nonexistent in the corresponding solid specimens. It occurs to the writer that the extraneous lines might possibly be obtained from the torn particles of the file. A magnetic separation on the powdered alloy specimens might clear up the diffraction patterns.

M. Hansen (*authors' reply*)—As the purpose of the investigation was only the determination of the two phase diagrams, no experimental information was obtained to quantitatively evaluate the effect of molybdenum and columbium additions on either: 1—the ductility of the titanium matrix, or 2—the solid solubility of impurities in the alloys.

Some qualitative deductions on the effect of these elements on the ductility of the titanium matrix can be made, however, from the results of preheat treatment deformation work. In general, molybdenum additions decreased the very good original ductility of both the iodide and Process A titanium. Alloys containing up to 34 pct Mo could be cold pressed at least to some extent, and alloys with more than 35 pct Mo could not be forged under the conditions used.

Columbium additions did not markedly decrease the ductility of the titanium lattice, as borne out by the facts that all alloys were easily deformed hot, and alloys containing up to 50 pct Cb could be cold worked to an 80 pct reduction in thickness. (Higher columbium alloys were not cold deformed.)

With regard to the extraneous low angle lines in the diffraction patterns, all samples were magnetically treated for removal of stray file particles prior to X-ray.

Solidification of Lead-Tin Alloy Droplets

DISCUSSION, M. Hansen presiding

H. M. Meyer (*Newark, N. J.*)—By dispersing the liquid, the heterogeneities present are isolated and most droplets supercool to solidify by homogeneous nucleation. However, a eutectic alloy contains the lead-rich crystal after the first solidification temperature. It should not supercool further, for the solid and liquid phases are in contact with each other. How can we speak, thermodynamically, of a "mild" catalytic effect where they, in fact, are supposed to react (even though two solid phases eventually form)?

J. H. Hollomon and **D. Turnbull** (*authors' reply*)—Upon cooling an alloy in any eutectic system in the absence of heterogeneities either one of the two phases may nucleate first. After the nucleation and growth of either the α or the β phase, the resulting solution is enriched in one of the components. Following the nucleation of, say, the α phase, the solution may become sufficiently enriched in β that it is then supersaturated with respect to the nucleation of the β phase. However, if the nucleation of β is completely catalyzed by α, β will form when the solution reaches the temperature and composition at which it is just saturated with respect to β. The α phase can be mildly catalytic in which case an intermediate supersaturation will be reached before nucleation of the β. In the Pb-Sn case, the tin-rich phase nucleates from a tin-rich solution (before the lead-rich phase nucleates) at a slightly lower temperature than that at which it forms when the lead-rich phase first nucleates. Thus lead has a mild catalytic effect on the nucleation of tin.

Constitution and Precipitation-Hardening Properties of Copper-Rich Copper-Tin-Beryllium Alloys

DISCUSSION, M. Hansen presiding

J. T. Richards (*The Beryllium Corp., Reading, Pa.*)—This interesting paper prompts several questions.

1—How do the authors account for the sudden increase in hardness of Fig. 14 between 64 and 128 hr? Either a double aging peak or precipitation of the ϵ phase could, of course, cause the increase; however, the authors have indicated that ϵ precipitation is a sluggish process. Data showing the course of the curves beyond 128 hr would be of considerable interest.

2—Have the authors an explanation for the differences noted in Fig. 21 between hardness and ultimate tensile strength curves? The increase in elongation and hardness coupled with the decrease in tensile strength for several of the alloys between 400° and 450° C suggests stress relief due to overaging at the grain boundary. Microhardness tests might prove helpful in following reactions at the boundary and within the grain.

3—Are data available indicating the effect of aging upon the elongation of cold-rolled alloys? It is probable that aging causes an increase in both the strength and elongation with some loss in formability.

4—Have the authors investigated the forming characteristics of strip rolled 50 to 87 pct reduction? It is anticipated that such material would have considerable directionality and low formability.

5—Do these alloys exhibit intergranular corrosion

Table V. Property Data for Several Heat Treated Cu-Sn-Be Alloys

Investigator	Reference	Composition, Pct (Bal. Cu)	Tensile Strength, Psi	Yield Strength, Psi	Electrical Conductivity, Pct	Rockwell Hardness	Elongation, Pct
Okamoto	10	2.0 Ni, 0.3 Be, 0.3 Sn			50	C21	
Hessenbruch	11	0.8 Sn, 0.3 Be	85,800		59		4.6
Konishi	12	2.0 Sn, 1.3 Be	114,000	90,000		C28	

after quenching from 700°C. This type of corrosion is one of the most serious production problems encountered in handling low beryllium alloys.

6—In addition to the property data shown, do the authors have proportional limit and endurance figures for any of the proposed alloys?

Table V lists composition and property data for several Cu-Sn-Be alloys from literature not mentioned in the paper. Although the authors found no published information on Sn-Be, Guertler and Pirani[1] previously reported solubility and property data for this system.

Perhaps the most serious drawback to alloys of the type mentioned in the present paper is their relatively high solution and cold-rolled strength and hardness. In commercial Be-Cu alloys, more efficient precipitation hardening means better formability in the unhardened condition for a given heat treated strength level.

It should be pointed out that Okamoto[10] and Hessenbruch[11] have found that Si, Mn, Al, Cd, Cr, Ni, Zr, or Cu additions are as effective as tin in hardening Be-Cu alloys of less than 1 pct Be. As indicated by Konishi,[12] however, there is always the possibility that Cu-Sn-Be alloys may provide a unique combination of strength and bearing qualities.

[1] W. Guertler and M. Pirani: International Tin Research and Development Council—Tech. Pub. No. 38, Series A (February 1927) pp. 22-39.

[10] M. Okamoto: Science Reports, Tohoku Imperial University (1942) 30, pp. 93-109.

[11] W. Hessenbruch: Zeits. Metallkunde (1936) 28, pp. 328-323.

[12] Y. Konishi: Kinzoku (1951) 1, pp. 13-17.

R. A. Cresswell and **J. W. Cuthbertson** (authors' reply)—The sudden increase in hardness between 64 and 128 hr shown in Fig. 14 is attributed to the precipitation of the ε phase. The evidence is that lattice strain resulting from the precipitation of this phase increases after annealing for 64 hr.

The apparent lack of agreement between the hardness and ultimate tensile strength curves in Fig. 21 may be due to the cause suggested, but there is an alternative, more probable explanation. At the higher aging temperatures there is a tendency for the precipitated δ phase to ball up at the grain boundaries with consequent increase in the elongation. A further point, which has some bearing on the discrepancy between the curves for the high tin, high beryllium alloys is that these alloys are two-phase in the solution-treated condition, and the presence of the second phase assists precipitation hardening.

No information is available on the elongation of cold-rolled alloys and on the resistance of Cu-Sn-Be alloys to intergranular corrosion. The forming characteristics of cold-rolled alloys have not been fully examined. Directionality effects were not observed, but intermediate annealing was necessary to enable large reductions to be taken. As one possible use of these new ternary alloys is for springs, it is intended to examine their fatigue and corrosion-fatigue resisting properties.

It is regretted that through an oversight no reference was made in the paper to the work of Guertler and Pirani. The authors were naturally aware of the work of these investigators, which was in fact carried out for the International Tin Research and Development Council. The importance of this work is fully appreciated but, owing to the form of the Sn-Be diagram as so far determined, the knowledge provided does not greatly facilitate the interpretation of the ternary system.

The figures quoted by Mr. Richards from the work of Hessenbruch and Konishi, respectively, are for alloys of very low tin content, and in the circumstances it is not surprising that the reported hardness values for the heat-treated alloys are far below those reported by us in Table IV for alloys containing 9 pct Sn or more. In view of the attention that has been drawn to the claims of Okamoto and Hessenbruch that silicon, manganese, and a number of other metals are as effective as tin in hardening Cu-Be alloys, we must point out that our investigation was primarily concerned with the effect of adding beryllium to Cu-Sn alloys and not with the effect of adding tin to Cu-Be alloys. The low tin alloys which we examined were primarily included for the purposes of determining the equilibrium diagram and the precipitation-hardening experiments were mainly confined to the higher tin alloys.

One object of our investigation was to find whether, by adding small amounts of beryllium to Cu-Sn alloys containing, say, 8 pct Sn or more, an alloy could be produced possessing the mechanical properties of commercial Cu-Be alloys containing much more beryllium. Our results have shown that the high tin ternary alloys compare very favorably in this respect with Cu-Be alloys and that they effect a saving of at least 70 pct in beryllium consumption.

Rapid Tempering of High Speed Steel

DISCUSSION, F. C. Hull presiding

P. K. Koh (*Research Laboratories, Allegheny Ludlum Steel Corp., Brackenridge, Pa.*)—On tempering steel by the induction heating method, a steep thermal gradient is generated from the surface inward. In order to heat the steel to the tempering temperature a short distance from surface by conduction, a quite high temperature is necessary on the surface, especially for such a rapid heating rate. One would wonder whether: 1—The authors ever found eutectic carbide on the surface of tempered tool. 2—How deep is the case within which the steel is properly tempered after a few seconds of induction heating? 3—Can the conditioning of the retained austenite be completed after only a few seconds at the tempering temperature? Did the authors

prove the complete transformation of retained austenite by X-ray diffraction patterns after brief induction tempering?

M. Cohen (*Dept. of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.*)—If rapid induction heating results in plastic strain, this phenomenon would provide a plausible explanation for anomalous acceleration of the tempering process in high speed steel as observed by the authors. However, it might be instructive to inquire critically into the role of rapid heating as a cause of plastic strain.

Rapid heating (or cooling) would not be expected to set up sufficiently high stresses for plastic strain in high speed steel unless steep thermal gradients are produced. For all practical purposes, thermal stresses and strains increase with the heating (or cooling) rate only insofar as rapid temperature changes are conducive to the generation of steep thermal gradients. This is particularly true, if the heating (or quenching) is applied from outside the specimen. In the case of induction heating, the heat is generated inside the specimen, but presumably it is concentrated in the outer layers and hence the conditions exist for enhancing the thermal gradients by fast heating rates. If the center of the specimen were to heat up nearly as fast as the exterior, thermal strains would be minimized. Thus, the occurrence of plastic deformation during induction tempering would seem to depend upon nonuniformity of heating as well as rapidity of heating.

A critical test of this hypothesis might be provided by the induction tempering of $\frac{1}{8}$ and $\frac{3}{8}$ in. rounds in comparison with the regular $\frac{1}{4}$ in. specimens. The power input could be adjusted to achieve the same heating rate in each instance (as indicated by the surface-welded thermocouple employed by the authors). Then it would be predicted, according to the plastic strain hypothesis, that the anomalous tempering rate will increase with the cross-section of the specimen.

A. E. Powers and **J. F. Libsch** (*authors' reply*)—In answer to Dr. Kuh, we wish to repeat that the temperatures were measured on the surface of the specimen and that the heating rates used were well below the maximum heating rate which the recording and controlling instrument can accurately follow. Although specimens induction-heated to the highest recorded tempering temperatures (1500 F) were not examined for partial transformation at this temperature, no transformation is indicated in the hardness and specific volume curves.

Hardness measurements along the cross-section of a $\frac{1}{4}$ in. specimen induction-tempered with an initial heating rate of 1300 F per sec revealed no measurable hardness gradients. In fact, this heating rate in a $\frac{1}{8}$ in. specimen also yielded no significant tempered hardness gradients. Our heating rates, although high, were not high enough to permit impractical temperature gradients.

By trading temperature for time we have endeavored to completely transform the retained austenite. Although we did not employ X-ray diffraction methods, our specific volume curves for the various tempering methods indicate that retained austenite is completely transformed at proper time-temperature parameter values.

We agree with Dr. Cohen that plastic deformation during induction heating may depend upon nonuniformity of heating as well as on rapidity of heating. Microstrain due to differing coefficients of thermal expansion of the various microconstituents and for the various crystallographic directions may also play a part. The relative importance of the two sources of strain is not known at present. Dr. Cohen's suggestion of using various sized specimens may be helpful in determining the mechanism of thermal strain.

Effect of Rate of Cooling on the Alpha-Beta Transformation in Titanium And Titanium-Molybdenum Alloys

DISCUSSION, F. C. Hull presiding

H. Margolin (*College of Engineering, New York University, New York*)—I should like to ask Dr. Duwez whether diffuse γ and β lines are obtained when Ti-Mo alloy powders are annealed longer than 3 min at 900 C before quenching in liquid argon.

P. Duwez (*author's reply*)—It is difficult to anneal a powder at 900 C in vacuum without considerable sintering. When such sintering takes place, filing of the sintered slug is necessary and diffuse lines are to be expected because of internal strain. Other experimental techniques should therefore be used in order to answer Dr. Margolin's question.

W. Rostoker (*Armour Research Foundation, Chicago*)—We were particularly interested in Dr. Duwez's paper because of our analogous work on the phase diagram and transformation rates in the Ti-Mo system. The phase diagram determined here[1] has already been presented and certain very obvious differences exist between ours and Dr. Duwez's results. The origin of these differences is obscure.

Concurrently with phase equilibria studies, work has been directed to a study of the transformation characteristics. The transformations of a supersaturated β phase may proceed either by a nucleation and growth process or by the time-independent, temperature-dependent reaction generally termed martensitic. The reaction kinetics may be conveniently summarized graphically on conventional TTT charts. The M_s temperatures were determined by a modified Greninger-Troiano method and the results show consistently lower temperatures than those reported by Dr. Duwez. A report of this work will appear in the very near future, and it is hoped a fuller discussion may be entered upon at that time.

P. Duwez—The author is very much interested in Dr. Rostoker's comments. The reasons for the discrepancies between the two Ti-Mo phase diagrams are not obvious. As far as the discrepancies in the M_s determinations are concerned, it is believed that the two techniques, namely thermal arrest and microscopic observation, might lead to measuring two different phenomena.

[1] M. Hansen, E. L. Kamen, D. J. Kenney, and D. J. McPherson: Trans. AIME (1951) 191, 6-383; JOURNAL OF METALS (October 1951).

Burst Phenomenon in the Martensitic Transformation

DISCUSSION, F. C. Hull presiding

H. Suzuki and **T. Homma** (*The Research Institute of Iron, Steel and Other Metals, Tohoku University, Sendai, Japan*)—Having dealt with the same subject in recent years, we read this paper with great interest. Throughout the paper some confusion seems to arise from disregarding the fact that there are two distinctly different mechanisms of propagation of the transformation in Fe-Ni alloys, one is the "Schiebung" and the other is the "Umklapp" transformation, as originally called by Forster and Scheil.[1] The latter type of transformation is observed as the remarkable phenomenon "burst" in the case of a coarse grained specimen. Under ordinary conditions the former takes place in alloys containing less than 29.5 pct Ni, while in alloys of higher nickel content the transformation of the latter type takes place. In Fe-Ni-C alloys, the boundary between two regions showing these distinct mechanisms is displaced to lower nickel concentrations, when the carbon content is increased. In the case of plain carbon steel the boundary corresponds to about 1.5 pct C. The two mechanisms do not always take place in accordance with the above-mentioned rule. For example, the Umklapp transformation is observed even in 25 pct Ni-75 pct Fe alloys when cooled over −40°C. Therefore, the quantity of martensite above the M_s point is not a characteristic one, but depends upon the nickel content and also on the rate of transformation. The apparent constancy of the quantity of martensite is caused by the fact that the Schiebung transformation takes place on the free surface at temperatures 10° to 20°C higher than in the interior of the crystal, while the nuclei of the Umklapp transformation cannot be formed at the surface.

In Fig. 12, the temperature of various types of $\gamma \rightleftarrows \alpha$ transformations are plotted against the nickel content. Alloys containing more than 35 pct Ni do not transform by means of the Umklapp mechanism even when cooled to −195°C.

The rate of propagation of the Schiebung transformation is slower than the Umklapp and, in the case of the former mechanism, providing artificial nuclei by means of a needle scratch, one can observe the propagation at as slow a rate as one wishes, if the experiment is carried out at a suitable temperature. On the other hand, artificial nucleation of the Umklapp could hardly be achieved even with such shocks as hammering. The martensite plates in Figs. 4, 5, and 6 of the paper seem to be formed by the Schiebung mechanism and that in Fig. 7 by the Umklapp mechanism. If the surface of the specimen had been continuously observed, and if the recooling had been carried out far more slowly, the continuous propagation of the plates *a*, *b*, *c*, and *d* in those figures would be observed.

The habit planes are different in the two mechanisms. In the case of the Umklapp they are {259} as measured by the authors and by Greninger and Troiano,[2] and in the case of the Schiebung they represent {225} habit. Moreover, in the latter case, the habit of reliefs at the free surface depends also upon the direction of the free surface. Hence there is some doubt that the planes in Figs. 4, 5, and 6 have the {259} habit.

For the theoretical considerations, in our opinion, the different mechanisms in the martensitic transformation cannot be understood by means of such phenomenological concepts as athermal nucleation, thermal nucleation, or strain embryo. It is also clear that the formation of the martensite nucleus and its growth cannot be well described in terms of motion of individual atoms, according to Fisher, Hollomon and Turnbull,[3] because the interaction between atoms is so strong that the "burst" takes place in the course of the transformation. The process can be described with better approximation by explicitly considering the motion of dislocations.[4] As easily seen from the incoherency of atomic arrangements at the surface of a martensite plate, there are rows of dislocations forming the boundary at the surface. Therefore a multiplication of dislocations must be required in the course of propagation of transformation, and the difference in the mechanism of multiplication results from the difference in the transformation mechanism. Thus the criterion of the occurrence of the burst is given by the conditions concerning the motion and formation of dislocations. In the case of the Schiebung transformation, the dislocations are multiplied in a manner analogous to that of ordinary slip, while in the case of the Umklapp the process resembles the deformation twin. It is unfortunate that the detailed description of the model of transformation and many experimental results consistent with this model must be reserved for the paper shortly to be published in Science Report of Research Institute of the Tohoku University.

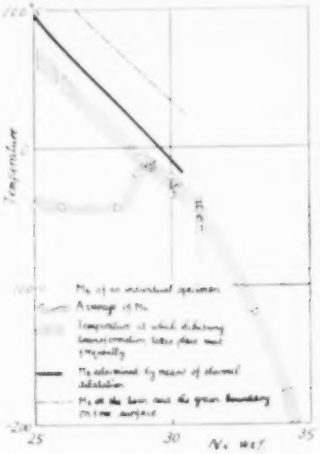
Temperature
Ms of an individual specimen
Average of Ms
Temperature at which shearing transformation takes place most rapidly
Ms determined by means of thermal dilatation
Ms at the bare and the grain boundary on free surface
25
30
35
Ni wt.%

Fig. 12—Effect of nickel on the gamma to alpha transformation.

E. S. Machlin and **M. Cohen** (authors' reply)—We are gratified to learn of the interest of Drs. Suzuki and Homma in the burst aspect of the martensitic transformation. Their Fig. 12 demonstrates that the burst temperature varies in a characteristic way with the nickel content, and that the phenomenon studied in the present paper is not an isolated case. We shall look forward to the publication of the rest of their results, together with a detailed explanation of the "Schiebung" and "Umklapp" models that they wish to apply to the transformation. At the present moment, it is difficult to assess the areas of agreement and disagreement between the discussers and the authors.

There are probably two (or more) ways in which martensite may propagate, one leading to the sudden formation of individual plates, and the other leading to gradual growth or thickening with decreasing temperature. Examples of the latter are the Au-Cd[5] and

[1] A. B. Greninger and A. R. Troiano: Crystallography of Austenite Decomposition, Trans. AIME (1940) **140**, p. 307.

[2] J. W. Christian: A Theory of the Transformation in Pure Cobalt, Proc. Royal Soc. (1951) [to be] A, p. 51.

In-Th" alloys. It appears from Fig. 12 that gradual

growth may also occur in Fe-Ni alloys containing less than about 29 pct Ni. Gradual growth was not observed in the authors' work, based on alloys containing 29.5 to 31.4 pct Ni. In this case, even the martensite formed above M_s was of the "sudden" type. The very thin plates *a*, *b*, *c*, and *d* in Figs. 5 and 6 and the thicker plates *e*, *f*, *g*, and *h* belong in this category, with the thicker ones comprising the main part of the transformation between M_s and M_f.

No habit measurements on the plates formed above M_s have been made, but there is no reason to suppose that the habit changes suddenly from {225} to {259} on passing through M_s. In fact, the plates *e*, *f*, *g*, and *h* look similar, except for size, to the very massive plates appearing below M_s (Fig. 7). However, the thin plates *a*, *b*, *c*, and *d* have a different appearance and may not conform to the {259} habit exhibited by the plates below M_s.

The significance of the martensite habit has been discussed in detail by the authors elsewhere.[7] Both the {225}[7] and {259} habits can be accounted for in terms of a double-strain mechanism involving two homogeneous displacements. Hence, it is not likely that the two habits typify such different processes as slip (Schiebung) and twinning (Umklapp) respectively. The discussers state that the former nucleates more readily at a free surface than in the interior of a crystal, while the latter does not. The authors have found that, both above and below M_s, there is preferential nucleation at surfaces. Moreover, contrary to the discussers' remark about artificial nucleation, both M_s and M_f may be raised by deformation.

The propagation of a martensite boundary by the dislocation mechanism of Christian[8] is not inconsistent with the concept of strain embryos. Christian's proposed multiplication of half-dislocations to explain the conversion of hexagonal close-packed cobalt to face-centered cubic cobalt is a particular model of a propagation process, but the prior presence of stacking faults is required to furnish the nuclei. In a similar sense, it is visualized that strain embryos provide the nuclei for the martensitic transformation under discussion here. If a dislocation mechanism can be suggested that accounts for: 1—the generation of {259} plates, 2—the corresponding mass movements, and 3—the final lattice relationships, one would still be concerned with the activation process that enables the propagation to start. The strain embryos enter the picture in this role.

[7] J. S. Bowles: The Crystallographic Mechanism of the Martensite Reaction in Iron-Carbon Alloys, *Acta Crystallographica* (March 1951) 4, 162.

Isothermal Formation of Martensite at Subzero Temperatures in a High Chromium Steel

DISCUSSION, F. C. Hull presiding

S. A. Kulin and **G. R. Speich** (*Atomic Power Div., Westinghouse Electric Corp., Pittsburgh*):—The authors have made a valuable contribution to the information available on the low temperature kinetics of the martensitic transformation. A similar study has recently been completed on a 14 pct Cr, 9 pct Ni, Fe-base alloy.[9] Extensive isothermal formation of martensite

[9] S. A. Kulin and G. R. Speich: Isothermal Martensite Formation in an Iron-Chromium-Nickel Alloy, *Journal of Metals* (March 1952) 4, 258; *Trans. AIME*, p. 258.

occurs in this alloy at subzero temperatures.

In conformity with the results obtained by the authors it was found that:

1—The amount of martensite obtained on direct quenching passes through a maximum with decreasing temperature of the quench. This is attributable to the "athermal" component of the transformation.

2—The initial rate of isothermal transformation goes through a maximum with decrease in temperature. However, it was found that the initial martensite content had no significant effect on the initial rate of isothermal transformation.

The conclusion that isothermal transformation is always preceded by some athermal transformation cannot be considered general since this was not found to be the case for the 14 pct Cr, 9 pct Ni, Fe-base alloy. In the latter alloy, isothermal martensite transformation takes place at temperatures above the M_s temperature.

B. S. Lement (*authors' reply*):—The possibility of isothermal formation of martensite in the 15 pct Cr, 0.7 pct C steel above M_s (−65°C) was investigated, but no definite evidence of this phenomenon was found. Although very small amounts of martensite were observed in some specimens held at −60°C for long times, this could not be confirmed as isothermal martensite because of difficulty of duplicating such results. If isothermal formation of martensite actually takes place just above M_s, the amount formed is probably less than 0.25 pct. On the other hand, no martensite was observed after holding specimens for long times at −50°C and above.

Isothermal Transformation and Properties of a Commercial Aluminum Bronze

DISCUSSION, F. C. Hull presiding

J. T. Richards (*The Beryllium Corp., Reading, Pa.*):—The mechanical property data listed in Table I and the test methods employed merit further consideration. The authors have reported excellent agreement between static and dynamic modulus determinations. As expected, the dynamic value generally exceeds the static modulus. This is probably due in part to the adiabatic characteristic of the dynamic modulus, which theoretically should exceed static or isothermal determinations. Rough calculations, based on the relationship:[7]

[7] L. Bergmann: *Ultrasonics* (1938) 10, pp. 418-419.

$$\frac{\Delta E}{E} = \frac{E_{ss} - E_{ds}}{E_{ds}} = \frac{2.39\,T\,E_{ds}\,\alpha^2}{10^7\,C_v\,\rho}$$

where T is the absolute temperature (°K); α, the coefficient of thermal expansion per °K; C_v, the specific heat at constant pressure (cal per g per °K); ρ, the density (g per sq cm); and E_{ds}, the isothermal elastic modulus (dynes per sq cm), indicate that the dynamic values should exceed static determinations for aluminum bronze by about 0.36 pct.

Of perhaps greater significance, however, is the role of stress, since the static value is evidently obtained at a considerably higher stress level than the dynamic determination. The increase in modulus resulting from dynamic tests ranges from 0 to 23 pct, with the smallest changes occurring in the high strength specimens. This agrees with the authors' statement that the harder materials produce stress-strain curves in which the lower portion approaches a straight line. In the other specimens, the nonlinear relationship between stress and strain causes a marked reduction in modulus at a stress level of one third the yield strength (based on 0.5 pct elongation).

Modulus values determined from the slope of the tangent to the stress-strain curve at one third the yield strength make comparisons difficult. It would be interesting to compare dynamic moduli with static values obtained from the tangent at zero stress. Do the authors have other modulus data available?

Although frequently employed in the copper and brass industry, yield strength obtained at 0.5 pct elongation is of doubtful design value since it does not provide a measure of plastic damage. In an extreme case, it is possible to have two materials of the same yield strength but different modulus wherein the proportional limit of one is at zero stress while in the other the entire specified 0.5 pct extension is performed elastically. This latter condition is generally the case in high strength materials, such as beryllium copper, so that the yield strength at 0.5 pct elongation falls below the proportional limit and consequently is always a function of modulus.

[9] J. T. Richards and E. M. Smith: Paper presented at the 1951 Annual Meeting, A.S.T.M.

M. C. Nickson (*London, England*):—The authors have made a valuable contribution to the literature on aluminum bronze and especially on the effect of an alloying element on the isothermal transformation of these alloys. Two points of interest arise however.

The aluminum content of the aluminum bronze investigated by the authors is high compared with those alloys which enjoy wider application in the heat-treated condition in this country, and one wonders whether such an aluminum bronze is ever heat treated in the United States. If not, there would seem to have been little advantage in investigating a commercial alloy of this high aluminum level. Little justification can be seen for the suggestion that the alloy chosen was equivalent to the eutectoid of the binary Cu-Al alloys because of the "negative replacement effect." Admittedly such an effect has been claimed by Dreher, but Yutaka and also Nishimura and Hisatune[10] indicate

[10] *Nippon Kinzoku Gakkai-Si* (1938) 2, (12) p. 597.

that iron has little effect on the aluminum content of the eutectoid. This is shown in their papers by the line representing the eutectoid composition being sensibly parallel to the Cu-Fe side of the isothermal section of the ternary diagram.

The writer also finds it difficult to accept the authors' account of the iron-rich particles. The authors take the view that the particles are body-centered cubic α iron. In this they are apparently supported by Yutaka, but the more complete investigations of Nishimura and Hisatune and Bradley and Goldschmidt[11] lead to a different view. According to these authors, α iron occurs only as a second phase in aluminum bronzes, and the iron constituent (variously named T or β_1), which occurs in the β alloys and their decomposition products, is an intermetallic phase with a variable composition within the range 20 to 27 pct Al, 25 to 45 pct Fe, balance Cu. It would be interesting to have more detailed information of the indirect evidence which the authors say they have that the particles are α iron in the present alloy.

[11] *Journal Inst. Metals* (1939) 65, (2) p. 389.

A. H. Kasberg and **D. J. Mack** (authors' reply):—The authors are aware of Mr. Richards' intense interest in the modulus and some of the interesting research he has underway to settle a few of the controversial considerations associated with the modulus and its determination, particularly in beryllium bronzes. The authors are, and were, cognizant of the questions which Mr. Richards has raised: 1—concerning the arbitrary choice of a yield strength based on 0.5 pct elongation and 2—the determination of the static modulus at a stress level of one third the yield strength.

It is our belief that despite the complete validity of Mr. Richard's arguments on both these items, our choice can be defended on the purely dogmatic basis that these values are extensively used by producers and consumers of aluminum bronze. However, Table II shows that the modulus is much higher when measured near the zero stress level on the stress-strain curves than when determined at a stress level of one third the yield strength (cols. 1, 2, and 3 are taken from the paper). These values determined from the stress-strain curves near the zero stress level give values in excess of the dynamic modulus. Granting that the modulus should increase as the stress level at which it is determined decreases, the results in the table seem unreasonable, although some similar large differences between static and dynamic moduli have been reported in the literature.[12] Before the results in the last column are appraised too critically, the inherent difficulties of the slope of tangent method at very low stresses such as used here should be kept in mind. Also, Froman,[13] and Evans and Wood[14] have shown that E increases very rapidly as the stress increases from 0, reaching a maximum value at 42.4 psi stress for steel and 56.6 to 424 psi stress for brass. The modulus then decreased gradually with further increase in stress until it reached the normal value. The values of E obtained at these very low stresses are 20 to 30 pct greater than the ordinary values. Ichinose[15] could not

[12] D. K. Froman: *Physical Review* (1930) 35, p. 264.

[13] R. H. Evans and R. H. Wood: *Philosophical Magazine* (1936) 21, p. 85.

[14] Masami Ichinose: *Proc. Phys. Math. Soc. Japan* (1941) 23, (2) pp. 119-131.

confirm these results although his load increments may have straddled the stress range in which this effect is observed.

Mr. Nickson has raised a question concerning the high aluminum bronzes used in this country. The alloy used in this study, Ampco 20, is a commonly used alloy for such things as knuckle joint bushings, cams and rollers, gibs, slides and welding jaws. It is always used in the quenched and tempered condition, as are all alloys lying beyond the α solubility limit.

Despite the phase diagrams of Yutaka and also Nishimura and Hisatune, which show that the eutec-

Table II. Modulus of Elasticity Under Various Stress Conditions

Specimen	Dynamic Modulus of Elasticity, 10^6 Psi	Static Modulus of Elasticity (at 1/3 the Yield Strength), 10^6 Psi	Static Modulus of Elasticity Near Zero Stress, 10^6 Psi
1A	13.5	11.8	15
1D	13.2	11.5	16.5
1E	11.4	9.5	10.5
5J	15.0	12.0	14.7

tool line parallels the Cu-Fe side of the diagram. It was found impossible to prepare an alloy that was entirely peritic unless the aluminum content was increased from 11.6 to 12.31 pct. This "negative replacement effect" is merely another way of saying that there is a partition of the solute aluminum between the two phases, face-centered cubic γ and the body-centered cubic α iron. Such a partition is well known for many ferritic alloys, particularly steels to which a carbide forming ternary element has been added. It was desirable to have a eutectoid alloy in this work to avoid possible complications from pro-eutectoid phases.

The indirect evidence which led the authors to suspect the particles were body-centered cubic α iron before Yuhasz's paper was located is: 1—the iron-bearing aluminum bronzes are slightly magnetic, the magnetism being directly associated with the number of visible iron particles. 2—the presence of carbon in aluminum bronze melts frequently causes a liquid miscibility gap which is suggestive of the Fe-Cu-C system. 3—the presence of iron causes a segregation during the freezing of alloys of eutectoid composition which leaves large areas of γ_2 in the structure of sand-cast specimens. These γ_2 areas disappear during the homogenizing heat treatment, thus suggesting a peritectic reaction which could be a projection of the Cu-Fe peritectic into the ternary Cu-Al-Fe system. It was also possible to calculate the composition of the iron-rich phase thus:

Composition of Cu-Al eutectoid	11.8 pct Al
Composition of Cu-Al-Fe eutectoid	12.3 pct Al

when 3.7 pct Fe is present (approximately) as in Ampco 20.

Then: 12.3 − 11.8 = 0.5 pct Al and $\frac{0.5}{3.7 + 0.5} \times 100 =$ 12 pct Al in the iron-rich phase. This composition was well within the magnetic α range of the Fe-Al system, very little Cu being present in the particles because Cu is only slightly soluble in body-centered cubic α iron.

Although the senior author was unable to electrolytically or otherwise extract the iron particles for analysis, thus confirming the indirect evidence, some work is currently underway that, it is hoped, will permit direct analysis of the particles.

Intermediate Phases in Ternary Alloy Systems of Transition Elements

By [illegible] Beck, E. A. Brand, E. C. Bain, and [illegible] A. Bice

DISCUSSION, J. T. Norton presiding

A. G. Metcalfe (Deloro, Ont., Canada)—The Co-Cr-Mo system has been investigated in the Department of Metallurgy, University of Cambridge, England, using the methods of thermal analysis and dilatometry. It was found that many of the phases in this system cannot be retained by quenching, so that methods of examination at temperature are necessary. However, Sykes and Graff were able to retain the σ phase in the Cr-Mo system by quenching, so that it is interesting that this phase does not appear in Fig. 3, as it does not decompose until 1200°C according to these authors. In alloys of more than 99.9 pct purity, we found the transformation to be at 1205°C. The advantage of the method of examination at temperature was demonstrated by the detection and investigation of a high temperature allotrope of cobalt.[1] This phase was found to be present in the 1200°C section of the diagram. The composition boundary of the α phase was not determined, but an alloy containing 53.3 pct Cr appeared to be in the α field at 1200°C, in agreement with Elsea, Westerman, and Mannino.[2] The question of purity appears to be of

[1] A. G. Metcalfe: Trans. Metal Metallurgical Congress, Detroit (1951).

[2] A. Elsea, A. E. Westerman, and R. K. Mannino: Trans. AIME (1951) 191, 1013; see also Trans. AIME (1949) 185, 305.

importance, as the cobalt used in the authors' alloys contained over 1 pct impurities. The shift of the α-phase field towards the cobalt corner would be expected to result in a corresponding decrease in the solubility of molybdenum in this phase, this appeared to be nearer 23 pct.

Alloys of high molybdenum content were not investigated in this work, and the R phase was not discovered. The existence of this phase and the phase in the Ni-Cr-Mo system is of great importance, and further details of its structure will be awaited with interest. One peculiarity seems to be that many of the α lines in the diffraction pattern are frequently more intense than the α_1 lines (e.g., see 3rd line from the line of spacing 1.246Å).

P. A. Beck (authors' reply)—Mr. Metcalfe is correct in stating that thermal analysis and dilatometry have the advantage of detecting transformations directly at temperature, without the necessity of quenching to room temperature. However, these methods are much less positive in identifying phases than the combination of X-ray diffraction and microscopy used in the present work. It is believed that the difference in the methods used at Cambridge and at Notre Dame has no bearing on the points raised by Mr. Metcalfe. That "many of the phases in this system (Co-Cr-Mo) can not be retained by quenching" is very doubtful. The only such phase specifically mentioned by Mr. Metcalfe is the new high temperature modification of cobalt, suggested by him. The existence and identity of this phase still remains to be confirmed by means of high temperature X-ray diffraction.

It is indeed quite possible that a high temperature transformation in cobalt, not suppressible by quenching, might have eluded us, since in the present work the immediate vicinity of the cobalt corner of the Co-Cr-Mo diagram was not investigated. The α alloys prepared (see Fig. 7) were calculated to locate the boundaries of α saturated with σ, R, and μ. Careful microscopic examination of these alloy specimens showed no trace of the familiar acicular structures usually resulting from not suppressible transformations, which take place on quenching. On the contrary, the specimens contained typical large equiaxed grains of α, which must have formed by grain growth at the annealing temperature of 1200°C. This suggests strongly that, at least in the composition range investigated, α is stable at that temperature.

The σ phase was definitely not detected at 1200°C, although this question was specifically investigated. As Mr. Metcalfe points out in his discussion, according to Sykes and Graff σ can be retained by quenching, so that here again, the use of quenched alloys does not account for the difference in results. It is quite possible, however, that differences in the impurity content of the alloys used may have shifted the peritectoid tempera-

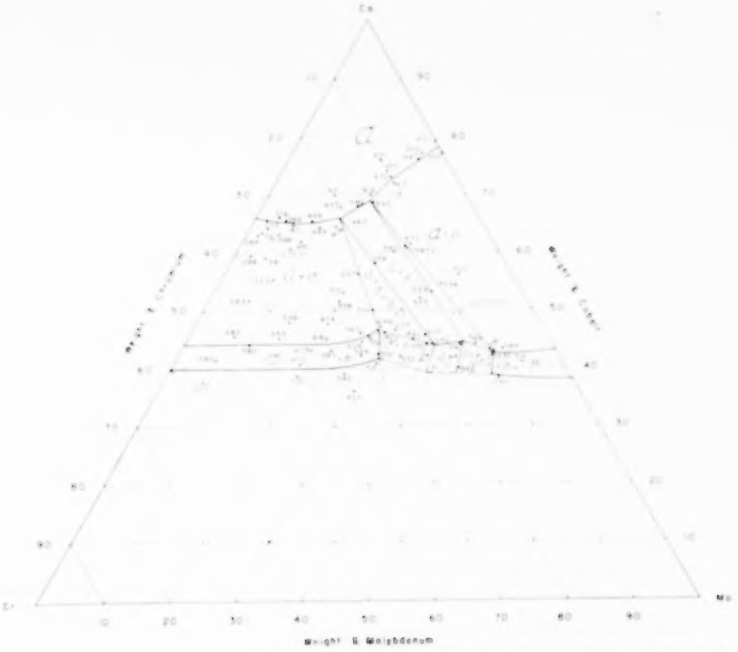

Fig. 7—1200 C isothermal section of Co-Cr-Mo diagram, with phase boundaries and the composition of ternary alloys used. Most binary alloys which were prepared are not indicated.

ture by 5 C or so, thus causing the slight discrepancy with Mr. Metcalfe's findings.

The suggestion that impurities in the cobalt may have caused a change in the (cobalt, chromium) σ phase boundaries from 52 to 55 to 56 to 60 pct Cr is quite unlikely. The major impurity in the cobalt used is nickel and, in accordance with Fig. 1 of the paper, the amount of nickel present (0.46 pct) is not expected to shift the cobalt-rich limit of σ by more than about 0.12 pct Cr, in contrast with the observed change of 4 pct Cr. The binary (cobalt, chromium) σ boundaries, located in the present work by means of 11 alloys of suitably chosen composition, are compatible with the values given in the paper by Elsea, Westerman, and Manning[7] within the limits of accuracy in the latter.[7] Mr. Metcalfe is apparently basing his conclusions on results with a single alloy.

[7] Personal communication from A. D. Elsea.

Chromium-Nickel Phase Diagram

DISCUSSION, J. T. Norton presiding

P. Duwez and **H. Martens** *(California Institute of Technology, Pasadena, Calif.)*—The results obtained by the authors lead to such a drastic departure from the generally accepted Cr-Ni phase diagram that it is felt that additional results should be presented before the new diagram is considered as being the correct one. In our laboratory, we have prepared a few alloys by melting in a helium arc furnace. Their structures were studied by microscopy and by X-ray diffraction, using the powder method with either chromium or copper radiation. The results are summarized in Table I.

No extra reflections were observed in the diffraction patterns, except for the 70 pct Cr alloy as melted. The few extra lines present in this pattern were apparently not the same as those given in Bloom and Grant's paper, and their interpretation is not clear yet. All the other results shown in the table are not in agreement with the diagram proposed by Bloom and Grant and can be explained by the old diagram, providing the solidus-liquidus lines are raised slightly on the chromium-rich side.

Table I. Phase Present Under Various Conditions

Cr Content, Wt Pct	As Melted	Homogenized At and Quenched From		
		2500 F	2300 F	2000 F
70	Chromium solid solution	Chromium solid solution	Chromium solid solution	Chromium solid solution plus nickel solid solution
50	Chromium solid solution		Nickel solid solution	
30 Cr	Chromium solid solution	Chromium solid solution		
30 Cr	Chromium solid solution	Chromium solid solution		

N. J. Grant and **D. S. Bloom** (authors' reply)—The authors feel as do Dawes and Martens that the proposed Cr-Ni phase diagram is not final, but we apparently have considerably more faith in it than they do. Perhaps the most pertinent point seems to be that they used powder samples instead of solid samples. The cold work through powdering could easily cause complete transformation of the high temperature phase to the low temperature phases. It is doubtful whether samples heat treated in a powdered state can be quenched with sufficient rapidity to retain the high temperature phase.

Whereas Dawes and Martens did not find evidence of the high temperature chromium phase, we wonder why in their 30 pct Cr alloys they do not show nickel lines in the as melted specimen, or chromium lines in the 2300 F quenched specimens. These lines should be present for the old phase diagram.

More recently, we have run thermal analysis curves on a very high purity chromium and have found rather good evidence of a phase transformation at 1840 C. The slope changes in the thermal analysis curves could be accounted for only by a transformation of this type. The oxygen content of this chromium was about 0.008 pct. We hope, nevertheless, that there will be other checks of the phase diagram in order to test its validity.

P. R. Kosting (*Watertown Arsenal Laboratory, Watertown, Mass.*)—This paper is important because it indicates that the Cr-Ni diagram might be quite complex. The purity of the chromium metal might affect the results of this work. More detailed information about the nitrogen content would be very helpful. In this connection H. T. Greenaway, of the Aeronautical Research Laboratories, Melbourne, Australia, has reported upon the freezing point of pure chromium and found it to be dependent upon the oxygen and nitrogen content. It was concluded that the freezing point of pure chromium with no nitrogen and oxygen is 1845 C ± 10 C. This freezing point for pure chromium is different from that given in the paper and indicates that further study of the properties of pure chromium is necessary.

N. J. Grant and **D. S. Bloom**—The purity of the chromium used in the determination of its melting point is undoubtedly a pertinent factor. The chromium which gave the value of 1930 C contained as known impurities: 1—about 0.02 pct C, 2—about 0.1 pct O, and 3—an insignificant quantity of nitrogen. These impurities in the above quantities would tend to lower the melting temperatures rather than raise it. Accordingly, impurity content would not explain a high melting point value.

An additional consideration is, of course, the accuracy of the thermocouple. Actually, later determinations of the melting point have indicated a temperature of 1900 C as being more nearly correct, the accuracy being no worse than about ± 15 C.

With regard to the value of 1845 C as reported by Greenaway, there are two points which must be considered: 1—This work was done in a hydrogen atmosphere and there are indications that liquid chromium can dissolve appreciable quantities of hydrogen. This hydrogen is largely released on solidification. 2—Beryllia crucibles were used to contain the chromium and the possibility of reduction of the beryllia by the hydrogen at these temperatures must be investigated. Greenaway made no mention of the beryllium content of the chromium. If silica was the binder for the beryllia crucible, it would be reduced very readily, resulting in silicon contamination and a significant reduction of the melting point.

Effects of Tungsten or Molybdenum Upon the Alpha-Beta Transformation and Gamma Precipitation in Cobalt-Chromium Alloys

DISCUSSION, J. T. Norton presiding

A. G. Metcalfe (*Deloro, Ont., Canada*)—The Co-Cr-Mo system has been investigated in the Department of Metallurgy, Cambridge University, England, and, although incomplete, the results may be of interest. Prior to the commencement of the work, it had been decided that only observations made at temperatures should be used in the construction of the constitutional diagram. The reasoning behind this decision was fully supported later by the publication, first, of the martensite-type transformation in cobalt,[1] and later by the observation at Battelle Memorial Institute that the σ-type phase appeared to decompose at elevated temperatures.[2] The detection of a high temperature allotropic transformation in cobalt[3] and its investigation over the Co-Cr-Mo system were possible by these means.

The alloys were of more than 99.9 pct purity, vacuum-melted and chill-cast under a pressure around 1 micron (mercury). These alloys were homogenized by about 44 hr heating at 1300° to 1325 C. The investigation was made by thermal analysis and dilatometry from 1000 C upward. The dilatometer curves were obtained at several rates of heating and the results were extrapolated to zero rate. The allotropic transformation in cobalt appeared to extend over a range of temperatures from 1119° to 1145 C. On the addition of chromium this rose to a maximum of 1323 C at the peritectoid,

$$\gamma\ (38\text{ pct Cr}) + \sigma\ (46\text{ pct Cr}) \rightleftharpoons \delta\ (39\text{ pct Cr})$$

where γ is the high temperature form of cobalt believed to be hexagonal and δ is high temperature form of the σ-type phase (authors' σ) termed σ (authors' γ) at lower temperatures. The replacement of chromium by molybdenum caused the transformation to occur at lower temperatures, e.g., an alloy with 34 pct Cr would transform from the σ to γ phase between 1270° and 1300 C, but on the replacement of 5 pct Cr by molybdenum the transformation temperatures were found to be from 1212° to 1234 C.

In Figs. 5 and 6, an attempt has been made to draw sections corresponding to those investigated by the authors. The dilatometric and thermal analysis methods of investigation are not so suitable for determining the positions of solid solubility boundaries

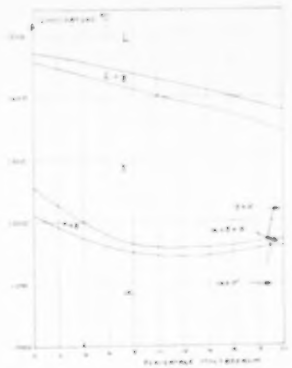

Fig. 5—Section of Co Cr Mo system at ratio Cr×100/Co + Cr = 20

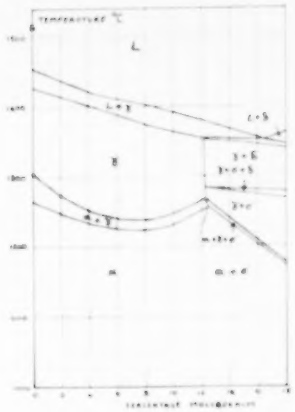

Fig. 6—Section of Co Cr Mo system at ratio Cr×100/Co + Cr = 32

as for detecting transformations, so that these boundaries must be regarded as tentative. However, Fig. 5 shows that some of the alloys plotted as α in Fig. 3 of the paper had been γ (the high temperature allotrope of cobalt) but had transformed back to α on quenching. A study of the isothermal transformation of γ cobalt to α cobalt has already been reported,[7] which showed that this would be expected. Fig. 6 gives the same information for the section starting at the 32 pct Cr alloy in the binary system. Here, it is interesting to note that another phase not retainable on quenching appears, with the transformation of δ to σ.

The significance of the α/γ transformation in connection with the erratic properties of Vitallium is not clear, at the moment. The mechanism of the transformation is not certain, and it is possible that the lines bounding the α plus γ region resemble the temperatures of M_s and M_f in the martensite transformation. If they represent the composition of α in equilibrium with γ, at any temperature (with the usual reservations for ternary systems) then annealing an alloy in the α plus γ range would result in the setting up of local regions differing in composition. This would certainly be expected to have a marked influence on the properties at lower temperatures, and it would be very interesting to know if the authors have observed any effects which might be explained in this way. Another factor which may influence the results is the slow rate at which γ cobalt decomposes to α cobalt at temperatures a little below the transformation temperature at zero rate of heating.[7] If the alloys should behave similarly, then precipitation of the α phase might well start from the γ solid solution in an alloy cooled from higher temperatures. The presence of about 0.5 pct Fe plus nickel may move the α plus γ region sufficiently for this to be the explanation of the results obtained in the up and down study on alloy MF.

W. Wilson, Jr. (*Armour Research Foundation, Chicago*)—For each composition, the authors determine the upper and lower temperature limits of the transformation range by plotting a chart of the percentage of α or β in a sample originally α and another initially β as a function of the aging temperature and "fitting" a straight line to the points. The upper and lower limits of the transformation range for each composition are read from the chart at its terminal points, e.g., 0 and 100 pct α.

A brief examination of the conditions necessary to obtain valid results by this method appears appropriate. For each aging temperature, two points for the percentage of α or β are found: one represents the percentage of α in the sample which was initially all α and the other, the percentage of α in the sample which was initially all β. The nucleation and growth rate of α from β and vice versa must be of the same order of magnitude, or the average will not be representative of the equilibrium percentage of α. In the absence of these conditions, the points representing either the samples initially of α or β might approach the equilibrium condition much closer than the average value. Hence the samples should be aged until the phase proportions in both samples are approximately identical.

A more recondite assumption of the method is the use of a straight line for extrapolating the results to 0 and 100 pct α. This assumption can be treated analytically by applying the lever rule. As a first approximation, straight lines may be used to represent the phase boundaries of α/α plus β and β/α plus β over the temperature range T_1-T_2. The straight lines might either be parallel or meet at some point (C_x, T_x). These possibilities are shown in Fig. 7, with the appropriate equations and quantities for each equation defined.

If the lines are parallel, the percentage of α is given by the equation

$$\text{Pct } \alpha = \frac{mT_{\alpha\alpha} - x_{\alpha\alpha}}{m(T_{\alpha\alpha} - T_{\alpha\beta})} - \frac{T}{T_{\alpha\alpha} - T_{\alpha\beta}}$$

where all of the quantities on the right side are constants except T. Hence the equation is linear, and the

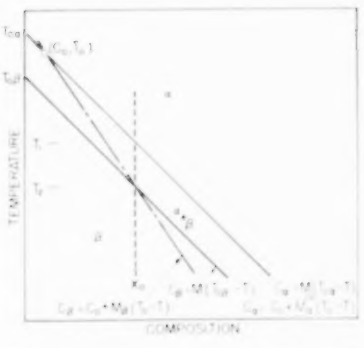

Fig. 7—Empirical equations for the transformation range boundaries

use of a straight line to determine the transformation range is a valid assumption.

If, however, the lines meet at some point, the percentage of α is given by the equation

$$\%\alpha = \frac{C - k_2}{(m_1 - m_2)(T - T_0) + m_1 - m_2}$$

where the quantities on the right are again constants except T. For this case, the equation is nonlinear, and the use of a straight line is an approximation except for very narrow temperature ranges. Hence, the use of a straight line for extrapolation may lead to errors in predicting the transformation range.

Similarly, the invalidity of the straight-line assumption can be demonstrated for any higher degree empirical equation fitted to the curves. Hence, the method cannot be relied upon to give an "accurate" prediction of the transformation temperatures, unless the curves for the temperature range can be approximately fitted by a pair of parallel straight lines.

E. F. Fletcher and **A. R. Elsea** (authors' reply): Regarding Dr. Metcalfe's remarks, several other investigators have claimed that there is a high temperature allotropic transformation in cobalt and cobalt-rich alloys which consists of a transformation from the face-centered cubic back to the hexagonal close-packed lattice. Consequently, throughout our investigation of cobalt-base alloys, we have been on the lookout for some evidence of such a transformation. Metallographic examinations have been made on specimens which have been heat treated for 100 hr at temperatures ranging from 600 C up to the melting point of the alloy, and in no case have we found evidence of any transformation other than the low temperature transformation from the hexagonal close-packed to the face-centered cubic lattice. This low temperature transformation is very sluggish because of the small energy change involved. If the reverse transformation occurred at a much higher temperature, this reaction would be expected to be sluggish also for the same reason, and, consequently, our metallographic and X-ray diffraction analyses should have indicated its presence. However, even though the transformations were not sluggish, with the result that the reverse transformation occurred upon cooling, the grain size of the alloy should be influenced by this transformation. Specimens heated slightly above the transformation should have a much finer grain size than those which were heat treated at a temperature somewhat below the transformation. No such variation in grain size was observed. In fact, the grain size became progressively coarser as the heat-treating temperature of the alloy was raised up to the melting point.

Metcalfe's investigation was made using thermal and dilatometric analyses from 1000 C upward, and all of the data were obtained from heating curves only. In addition to this, no X-ray diffraction analyses were made to positively identify the phase present. In view of the sluggish nature of the α–β transformation which occurs below 1000 C, there is a strong tendency for the apparent temperature of the transformation to be displaced upward, especially when only heating curves are used. This is shown clearly by the work of Wever, Haschimoto, and Lange on the Co–Cr binary system. In their work the hexagonal close-packed to face-centered cubic transformation on heating was displaced upward by as much as 250 C, while the apparent transformation on cooling was suppressed by as much as 600 C. Thus, for some of their alloys, the difference between the transformation temperature observed on heating and that observed on cooling was as much as 850 C.

With regard to Mr. Wilson's comments we would like to point out that very early in this investigation of cobalt-base alloys, we determined the rate at which α transforms to β and the rate at which β transforms to α. We found that although they are not identical they are of the same order of magnitude and for our purposes the difference could be ignored. That is the reason we have felt free in using the average structure of two specimens, one initially α and the other initially β before the aging treatment. We are also aware of the fact that a straight line cannot be used to represent the relationship between the percentage of the phase present at different aging temperatures if the boundaries of the two-phase region are not parallel straight lines. However, when the upper and lower boundaries of the two-phase region are approximately parallel curves with a large radius of curvature, this method of plotting the data can be used without introducing an appreciable error. This is especially true if the amount of one phase present is small, as it was in the case of most of our specimens.

Structural Studies of Plastic Deformation in Aluminum Single Crystals

DISCUSSION: W. L. Fink presiding

E. A. Calnan (*Metallurgy Dept., National Physical Laboratory, Teddington, Middlesex, England*): At the time of publication of Chen and Mathewson's paper a very similar investigation was being completed at the National Physical Laboratory. Back-reflection Laue patterns and optical observations were made on single crystals of super pure aluminum subjected to simple tensile deformation. The results of the determination of the plane of the deformation bands (here referred to as "kink" bands), the asterism on and between bands, and the interpretation of this asterism as rotation about the approximate [211] direction, are in complete agreement with Chen and Mathewson. There is one important difference in reference to their description of the "bunching of slip lines." An apparently similar feature, of which a particularly clear example is shown in Fig. 19, was observed in all the crystals examined, but it was found that the edges of the bunches (or "striae") were not quite parallel to the slip lines. That is to say, lamellae of much and little slip developed which were not quite parallel to the primary slip plane, Fig. 19. Within the striae which varied considerably in prominence and width, evidence of a second operative slip system could be observed, even after only a few percent extension. This took the form of slip lines, Fig. 20, or what appeared to be a complex of kink bands, depending on the orientation of the surface. The additional system was that of second highest resolved shear stress for the particular stress axis orientation. The pronounced difference in asterism which results when the X-ray beam overlaps one such stria is seen by comparison of Figs. 21a and b. It seems that these striae are the deformation bands described by earlier workers[7] as regions where different slip systems are operative and which are of

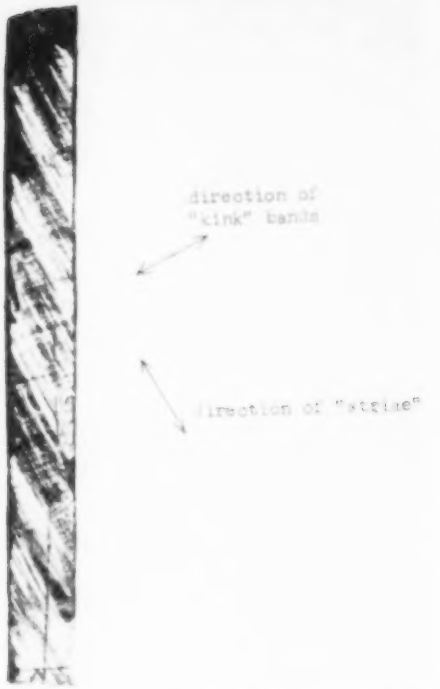

Fig. 18—Single crystal of super pure aluminum showing "kink" bands and "striae" 4 pct extension. X3

Fig. 19—Single crystal of aluminum showing "kink" bands and striae. 4 pct extension. X50.
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rsurse quite distinct from the kink bands reported by Honeycombe,[7] Cahn,[8] and Chen and Mathewson. Figs. 18 and 19 show that both types, however, can appear in the same crystal and as such both contribute to the

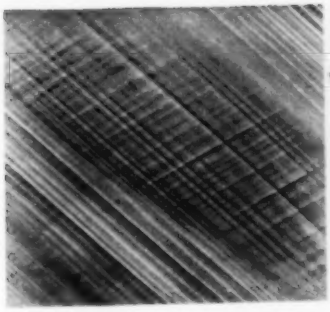


Fig. 20—Second slip system operative within a striae. 9 pct extension. X500.
Area reduced approximately 50 pct for reproduction.

Fig. 21a—Back reflection Laue pattern with X ray beam not overlapping striae. 13 pct extension.
Area reduced slightly for reproduction.

Fig. 21b—Pattern with X ray beam overlapping a prominent striae. 13 pct extension.
Area reduced slightly for reproduction.

asterism. The details of this investigation will be published elsewhere.

[7] C. S. Barrett and L. H. Levenson: Trans. AIME (1940) 137, p. 112.
[8] R. W. K. Honeycombe: Trans. AIME (1950) 188, p. 1009; Journal of Metals (August 1950).
[9] R. W. Cahn: Journal Inst. Metals (1951) 79, p. 129.

H. Wilsdorf and **D. Kuhlmann-Wilsdorf** (*National Physical Laboratory, South African Council for Scientific and Industrial Research, Pretoria, and Dept. of Physics, University of Witwatersrand, Johannesburg, South Africa, respectively*)—In this very stimulating paper the discovery of slip-band clusters is of special interest. This is particularly so because the effect apparently does not exist in aluminum of lesser purity because otherwise it would most probably have been

found long ago. We believe that the effect of geometrical softening, as described by Andrade and Roscoe,[3] is the cause of the slip band clusters in α brass, but this does not seem to be true for aluminum, or in any case it can be a contributory factor only.

We recently investigated two aluminum crystals, one oriented near [100] the other near [111], which showed marked slip-band clustering. While the former exhibited no deformation bands, in agreement with the findings of Chen and Mathewson, the latter showed a great number of uncommonly fine and closely spaced bands, Fig. 22. With respect to the authors' considerations on the mechanism of deformation band production, we are interested to learn whether the existence of these short deformation bands within the clusters may be in serious disagreement with their theory.

A close examination of the regions between the clusters after moderate or large deformations reveals that in them the surface is rumpled. These rumplings are caused by a multitude of wave slip bands. Electron micrograph photographs show that in spite of their macrocrystallographic appearance, they in reality are formed by exceedingly fine multiple slip, Figs. 23 and 24. The very fine lines visible beside the actual slip bands belong to a structure which was discovered recently[4] and which was called "elementary structure." A more detailed paper on our observations is to be published.

3. E. N. da C. Andrade and R. Roscoe: *Proc. Physical Soc.* (1937) 49, 70.

4. U. Kimoto and H. Kanzaki: *Nippon-kinzoku-gakkai-shi*, 1951, 15, 307.

E. R. Hasiguti (*Dept. of Metallurgy, Faculty of Engineering, University of Tokyo, Tokyo, Japan*).—It is quite satisfactory to find that many of the authors' results reported in this paper agree very well with ours. But I should like to make a brief comment on the problem of rotation of deformation bands.

As the authors have pointed out, the deformation bands rotate toward the stress axis as the crystal elongates. The question is whether this rotation is the purely geometrical result of the glide process of single crystals or not. If it is purely geometrical, we can calculate the angle of rotation of the deformation band from geometrical consideration of the glide process. But if this is not the case, we have to seek for other causes of rotation, e.g., the traveling of bend planes through the crystal, etc.

I have derived a formula expressing the relation between the rotation of the deformation band and that of the slip band, assuming a purely geometrical relationship, the details for which will be published later. The formula is as follows:

$$\cot\alpha = \frac{\sin(\chi_1 - \chi_0)}{\sin\chi_1 \sin\chi_0} \qquad [1]$$

where χ is the angle between the stress axis and the slip direction; χ_1 the angle between the stress axis and the slip plane; α the angle between the slip plane and the plane of the deformation band; and suffixes 0 and 1 indicate before and after extension, respectively. This formula was tested in our laboratory with fairly successful results; so we may conclude that the rotation of the deformation band is the purely geometrical result of the glide process of a single crystal.

The authors gave an experimental angular relation between the deformation band and the slip band in Fig. 13 of their paper, from which we get $\chi_0 = 44°$, $\chi_1 = 36°$, and $\chi = 36°$. Substituting these data in eq 1, we get

$$\alpha = 76°$$

which means a rotation of 10° of the deformation band toward the stress axis. This result agrees quite well with the authors' measurement given in Fig. 13, although we cannot make a strict comparison, since the authors did not give the pole of the plane of the deformation band. I shall be very glad if the authors will check the above formula with their available data.

N. K. Chen and **C. H. Mathewson** (authors' reply).—We are glad to learn that our results have been generally confirmed by Mr. Calnan. The difference he pointed out, with reference to the formation of clustered slip lines, is of special interest. However, without a detailed description of his experiment, especially regarding dimensions of specimens, rate of deformation, and documentation of crystal orientations, a comparison of his results with the ones reported in this paper would seem difficult. If, judging from Fig. 18, the specimen was only about 0.5 cm in one of the cross dimensions perpendicular to the stress axis, a

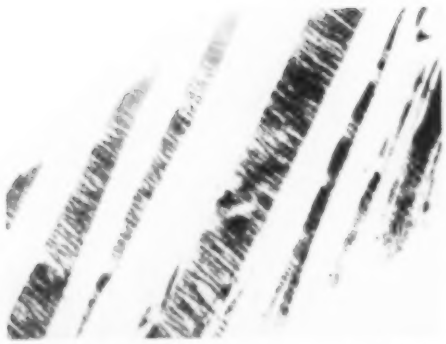


Fig. 22—Crystal oriented near [111] after a shear of 0.41 exhibiting pronounced slip band clusters with numerous short deformation bands.

Fig. 23—Electron micrograph showing wavy slip bands. 2000:1.

Fig. 24—Detail from Fig. 23. SiO replica shadowed with tungsten oxide. Photographic negative 11,000:1.

fundamental difference in the appearance of slip lines due to specimen size would be expected." Moreover, if the rate of deformation were comparatively large, as would generally be the case in testing single crystals of smaller size, a predominance of slip clusters would also result, as previously demonstrated by Crussard.[7]

[7] C. Crussard, Slip in High Purity Aluminum Crystals, Revue Metallurgie (1949) 45, p. 288.

The strain rate effect is now being investigated by one of the authors using small aluminum single crystals (⅛ in. in cross-section x 1 in. long in gage length) extended in a specially designed macrotensile machine. The so-called "striae," or clustered slip bands, were observed in certain crystals when the deformation was quite fast (above 0.003 in. per in. per sec); whereas no such "striae" were observed in other crystals when the strain rate was below 0.0003 in. per in. per sec. Intermediate cases were also observed where slip bands just began to show clustering. Thus, the formation of deformation bands and the participation of a second slip system (premature conjugate slip and/or the cross-slip), although direct consequences of certain fundamental lattice rotations during deformation, may be expected to vary in their distribution or predominance, according to the experimental conditions. An orientational effect, as found in the present investigation with respect to the formation of deformation bands and the characteristic appearance of slip lines, may very well be masked if the experimental conditions are substantially changed.

It is agreed that the apparent deviation of the general direction of "striae" observed under low magnification from that of the component slip lines may have resulted from unequal amounts of shear in the different slip lamellae. However, in order to clarify "striae" of this kind of deformation bands in the earlier sense, further work would be needed to establish their special characteristics, such as the gradual development of an orientation difference between band and matrix, and an unchanging width of the band during progressive deformation. Incidentally, Mr. Calnan's Fig. 21b, when superimposed on Fig. 21a gives almost the same orientation in spite of the fine structure associated with each spot. This is in conformity with the findings stated in the present paper that "X-ray photograms taken on and between areas with clustered slip bands represented the same orientation." It would be of interest to look into the possibility of polygonization of aluminum at room temperature or fragmentation as a probable cause of the spottiness in the present case.

With regard to the discussion of Drs. Wilsdorf and Kuhlmann-Wilsdorf, we may refer to the earlier work by Collins and Mathewson[8] who found deformation bands in extended aluminum single crystals of a lesser purity. With reference to Fig. 22, in the case of short deformation bands entirely within the slip clusters, our mechanism of band formation could be used in explanation if the bending of each slip lamella were considered to be a unit process. In such case, deformation bands may not necessarily cross the entire crystal.

Dr. Hasiguti's formula, expressing the relation between the rotations of deformation bands and slip bands on a purely geometrical basis, could be well used as a first approximation in locating the deformation bands in our experiments (see Fig. 16 of the paper). However, as pointed out in the paper, other factors, such as formation of new bands, action of "bend planes," and the strain hardening associated with increasing deformation would always be present to prevent the simple rotation of the bands in this purely geometrical sense. Further work seems needed to clarify this point.

Effect of Alloying Elements on the Elevated Temperature Plastic Properties of Alpha Solid Solutions of Aluminum

by O. D. Sherby, T. A. Trozera, and J. E. Dorn

DISCUSSION, W. L. Fink presiding

W. L. Fink (*Aluminum Research Laboratories, Aluminum Co. of America, New Kensington, Pa.*)—How do the authors account for the fact that true stress-true strain curves were obtained as shown in Figs. 5 through 8 beyond the point of maximum load? Would it not be expected that the specimens would begin to neck at this point?

J. E. Dorn (authors' reply)—We wish to thank Dr. Fink for this additional opportunity to discuss the criterion for necking under tensile straining. Although local plastic deformation resulting in necking invariably starts at the strain coincident with the maximum tensile load at temperatures below those at which recovery occurs, at higher temperatures tension bars can be strained well beyond the strain at the ultimate strength without incidence of necking. Thus a true tension stress and strain can be evaluated well beyond the point of maximum load as shown in our data. Analogously creep specimens often retain a uniform cross-sectional area over the gage length much beyond the strain at which the tertiary stage of creep begins.

Although a decreasing load with strain appears to be a necessary criterion for local plastic flow, the quoted high temperature data reveal that it is not, per se, a sufficient criterion. For example when plastic deformation is nonhomogeneous over the length of the bar, the weakest section strains and, if the ultimate strength is exceeded, this section remains weakest and therefore continues to deform, resulting in a reduced section or neck. But if the deformation is homogeneous, as in a specimen of wax or tar, all parts of the gage section strain uniformly. Consequently the straining remains homogeneous even though the load be decreasing. In the case of metals, the more homogeneous strain at elevated temperatures may not necessarily result from the absence of crystallographic mechanisms of flow (as is true for waxes) but might also be associated with the effect of the strain rate on the flow stress. Perhaps at elevated temperature when the weaker sections begin to flow faster, their resistance to stress increases causing some other sections to now flow faster, thus reducing the tendency toward continued local flow at one section. Since the strain rate effect is small at low temperatures, this phenomenon is inoperative, and necking is observed at the strain for the ultimate strength.

Effect of Alloying Elements on the Electrical Resistivity of Aluminum Alloys

DISCUSSION: W. L. Fink presiding

M. K. B. Day and **H. W. L. Phillips** (*Research Laboratories, British Aluminium Co. Ltd., Gerrards Cross, Bucks., England*)—In the description of their experimental procedure the authors state that, since the temperature coefficient of resistivity of dilute alloys is known to be practically independent of composition, a temperature correction of 0.00429 microhm cm per °C was applied to the results obtained for each alloy.

The results of an investigation completed in these laboratories in May 1940 on the physical properties of a series of commercial wrought aluminum alloys of compositions comparable with some of those used by the authors indicated that the temperature coefficient of resistivity for an alloy was dependent upon its actual resistivity. Our experimental results are plotted in Fig. 5.

Fig. 5—Dependence of temperature coefficient of resistivity upon electrical resistivity of aluminum alloys.

A. T. Robinson (*authors' reply*)—The results of the investigation by Day and Phillips on the temperature coefficient of resistivity for commercial wrought aluminum alloys are quite interesting. At the time of our experiments, we were quite concerned about the contradictions existing in the literature regarding this coefficient. For this reason we conducted all tests within a narrow temperature band of 22° to 26° C and corrected to 24° C, which made the maximum temperature correction only 2°C.

By using a temperature coefficient of resistance of 0.0043 microhm cm per °C as suggested by data of Day and Phillips for our highest alloy (1.617 atomic pct Mg and having a resistance of 3.520 microhm cm) instead of 0.00429 microhm cm per °C given for 99.996 pct Al, the corrected value would be changed by 0.002 microhm cm for a 2°C correction. This difference is less than the sensitivity of the Kelvin bridge for the range used and is considerably smaller than the errors due to measurements and other sources.

Though the coefficient of resistivity is not critical in our analyses, we do believe this property to be quite significant and are looking forward to the publication of this fine contribution by Day and Phillips.

Creep Characteristics of Some Platinum Metals at 1382°F

DISCUSSION: W. O. Binder presiding

R. Lowrie (*N.A.C.A. Lewis Flight Propulsion Laboratory, Cleveland*)—With regard to the considerable strengthening in creep of deoxidized palladium caused by annealing for 1200 hr in air, may I suggest that this was caused by internal oxidation of the residual aluminum. Meijering and Druyvesteyn¹ in a comprehensive investigation of internal oxidation of silver, copper, and nickel alloys demonstrated that the production by internal oxidation of a very finely dispersed oxide phase was accompanied by a large increase in hardness. In their only experiment on creep of an internally oxidized material, they found a much higher creep rate for the unoxidized alloy (1 At.% Be in silver) than for the internally oxidized material.

The two necessary criteria for hardening a solid solution by internal oxidation of one component as advanced by Meijering and Druyvesteyn are that the affinity of oxygen for the solute must be sufficiently greater than its affinity for the solvent, and that the oxygen must diffuse more rapidly in the solvent metal than does the solute. The first condition, which assures oxidation of the solute in preference to the solvent metal, is certainly met by the Pd-Al alloys. I believe there to be no information available on the rates of diffusion of aluminum and oxygen in palladium. However, the diffusion coefficients of oxygen in silver and copper are larger by a factor of 10^7 to 10^9 than those of metallic solutes in these metals at the same temperatures. Thus, it appears probable that the Pd-Al system also satisfies the second condition. In view of these facts and of the authors' observation of a subscale, it appears very likely that hardening by internal oxidation is responsible for the great improvement in the creep behavior of palladium brought about by long annealing in air.

Furthermore, internal oxidation will explain the fact that the creep rate of the annealed specimen after 1200 hr of testing is less than that of the virgin specimen tested for 1200 hr and, likewise, the authors' statement that the secondary creep rate of the annealed specimen may be less than that of the virgin specimen. Inasmuch as the annealed specimen has had a 2400 hr oxidation treatment after 1200 hr of testing, a greater

fraction of its cross-sectional area will have been strengthened, and it should be stronger than the virgin specimen for all times of testing until both specimens have been completely penetrated by internal oxidation. A rough calculation, based on a penetration of 0.055 in. in 3000 hr, shows 40 pct of the area to have been oxidized in 1200 hr and 55 pct in 2400 hr.

Any of several simple tests might be made to check the conclusion that internal oxidation caused the observed effect. The authors mention having made hardness tests. The hardness, preferably determined by a microhardness test, of the subscale should be considerably higher than that of the unoxidized material at the core of the bar. Direct evidence of the influence of internal oxidation on the creep rate could be obtained by annealing a bar for 1200 hr in a vacuum and testing it in creep, or by testing a virgin bar in creep in an inert atmosphere. Comparison of the creep curves of these specimens with those of the specimens tested in air or annealed and tested in air should conclusively show the effect of internal oxidation on the creep of palladium.

The authors are to be commended for their recognition of the possible influence of annealing upon the creep strength of palladium and for their decision to employ one of their precious specimens to test this influence. This has made possible a rational explanation of the creep behavior of deoxidized palladium and points out an experimental variable to be regarded seriously in other work with such materials.

R. H. Atkinson and **D. E. Furman** (authors' reply).—The authors note, with interest, the suggestion by Mr. Lowrie that the improved creep performance of palladium caused by prolonged annealing in air may be due to internal oxidation of residual aluminum. While the authors agree that internal oxidation undoubtedly occurs, they would point out that the amount of residual aluminum was quite small and that the prolonged anneal had very little effect on the hardness (Vickers) as measured with loads of 1 and 5 kilos. Microhardness measurements were made on a section of a bar after a creep test. There was some local hardening but it was slight (only 5 points) and was restricted to a peripheral zone about 0.05 in. thick. Most of the subscale area had the same hardness as the center of the bar. Another bar was retested after most of the subscale zone had been removed; the creep rate was of the same order as it was before the subscale layer was removed, indicating that there was no substantial difference in creep strength between the latter and the rest of the bar. It would appear, therefore, that the reaction responsible for the improvement in creep resistance had already proceeded to completion throughout the cross-section of the bar. In the circumstances the authors remain of the opinion that the improvement effected by the extended anneal may be due to its affording an opportunity for the subsurface reaction to reach equilibrium before the load was applied.

Our observations indicate that Mr. Lowrie is probably correct in his assumption that oxygen diffuses more rapidly than aluminum in palladium. After the creep test of one of the bars had been concluded, successive layers, 0.005 in. thick, were turned off and examined spectrographically. No difference could be detected between the aluminum content of the surface layer and layers at depths of 0.020, 0.035, and 0.075 in. below the surface. In other words there was no spectrographic evidence of measurable diffusion of the aluminum after more than 4000 hr at 750°C. With regard to the diffusion of oxygen in metallic palladium, although the rate of diffusion has not been measured, there is indirect evidence that diffusion occurs readily at high temperatures.

Creep Behavior of Zinc Modified by Copper in the Surface Layer

DISCUSSION, W. O. Binder presiding

J. C. Fisher (*General Electric Research Laboratory, Schenectady*).—The experimental results described in this paper can be interpreted in at least two ways based upon the dislocation model of slip. It is possible that dislocations are generated in the interiors of zinc single crystals and that the presence of a thin copper plate prevents them from passing out. On the other hand, it is possible that most dislocations are generated at the free surfaces and that a thin copper plate interferes with the generation process. I believe that the second possibility is the more plausible.

It is fairly well accepted that the dislocations responsible for slip are generated at defects of the type described by Frank and Read.[1] Each such defect, called a Frank-Read source, can produce a large number of dislocation loops when a stress is applied to a crystal. A Frank-Read source in the interior of a crystal is a segment of dislocation line pinned at both ends, lying in a glide plane, and having its Burgers vector in the glide plane. For resolved shear stresses less than a critical value τ^* the equilibrium shape of the segment is an arc passing through the pinned ends and having greater curvature the higher the stress. For resolved shear stresses higher than τ^* there is no equilibrium shape, and successive dislocation loops are generated. The critical stress τ^*, corresponding to a semicircular arc of dislocation line, is given by the equation

$$\tau^*/G = b/L$$

where G is the shear modulus, b, the magnitude of the Burgers vector (generally about 1 atomic diam); and L, the distance between the ends of the generating segment.

The dislocation loops generated by an interior Frank-Read source move concentrically toward the surface of the crystal. If the outermost loop meets an obstacle of some sort, additional loops pile up behind. They, in turn, multiply the force on the outermost loop by n, where n is the number of piled up loops. n can be in the neighborhood of 10 to 100, and unless a thin copper plate can act as a nearly impenetrable barrier, slip should proceed with little hindrance if interior Frank-Read sources are its cause.

There is reason to believe that surface Frank-Read sources can be responsible for slip single crystals. Consider a dislocation segment that is pinned at one end, the other end terminating upon the surface of the crystal. Because of line tension, the free end of the segment always will be normal to the crystal surface. It is evident then that a surface source can be thought of as pinned to a point outside the crystal. The exterior point is a mirror image of the interior pin point across the free surface. The effective length of a surface source

where d is the crystal diameter, t, the thickness of the surface layer, χ, the initial angle between the major axis of the slip ellipse and the cylindrical axis of the specimen, and S, the shear resistance of the surface layer. The shear stress on the slip plane of the crystal is then reduced by $4tS/d$. A conservative calculation, using only the initial thickness of the copper film and a shear resistance (for copper) of 10,000 psi, gives a figure of 0.6 psi for the reduction of shear stress due to the surface layer. Then, using the test plotted in Fig. 4 (where the change in the creep rate after deposition of the copper can be estimated), the surface layer may be supporting 0.6/26.5 or 3 pct of the applied stress. Although this is not large enough to account for the sevenfold decrease in rate shown in Fig. 4, it does indicate that the strength of the surface layer is significant in these experiments.

The existence of different rates of temperature dependence of plated and unplated zinc crystals does not exclude the mechanical resistance of the surface layer as an important factor in these experiments, since the properties of the surface layer may change with temperature.

An attempt was made to estimate the extent of the diffusion occurring in the surface layers during the test, based on an assumed period of 1 hr from the time of deposition of the copper to the time the creep rate attains its final, fairly constant value. However, it was necessary to use highly extrapolated diffusion coefficients for low zinc alloys, and the results were not consistent with the authors' visual observation of appreciable diffusion at all test temperatures. We are unable, therefore, to refine our estimates of the effective thickness of the surface layer and of its resistance to deformation. However, both would be expected to increase as diffusion takes place and the contribution of the mechanical resistance of the film would then be higher than calculated above. With the data available, we can only say that this contribution would be at least a significant one.

It may be of interest to note that results of some work at Columbia University on the effect of films of synthetic plastics on the creep of cadmium single crystals are consistent with the interpretation that the effect of the plastic films on the creep rate is due primarily to the mechanical resistance of the film.

Creep and Stress Rupture Behavior of Aluminum as a Function of Purity

DISCUSSION: W. O. Baeder presiding

C. S. Roberts (*The Dow Chemical Co., Midland, Mich.*): The authors have completed a fine study of the creep process, showing fundamental significance and well-conformed scope. As a result of a careful correlation between rates, fracture types, and structural observations, the validity of the equicohesion range concept has been proved for aluminum.

However, I must question their interpretation with respect to the effect of impurities on the sharpness of the transition. It is regrettable that the authors did not conduct the creep tests over the entire temperature range with the fine-grained, high-purity aluminum. This would have allowed a comparison with the impure alloys independent of a grain size effect. The transition stress and minimum creep rate, which are strongly dependent on impurities, appear to be relatively independent of the grain size in the range investigated. An influence of grain size on the sharpness of transition might be expected, however. The relative amounts of grain boundary area and grain volume should have an effect on the amount of the minor deformation process necessary to allow operation of the major process on either side of the transition.

The data obtained at 500°F and shown in Fig. 4 allow a judgment of the grain size effect. If the angle between the linear segments is used as a criterion of sharpness of transition, the more marked effect appears to occur in the fine-grained material. In Fig. 6, the data at 900°F for fine-grained specimens show a less marked transition for the more impure 3S than for the 2S specimens. With such results as these, the authors' explanation of impurity effect as shown schematically in Fig. 22 appears questionable.

Finally, I should like to compare the authors' results with some of those from creep studies by Crussard[1] on high purity aluminum (99.995 pct). He found transi-

[1] C. Crussard: *Revue Metallurgie* (1946) 43, p. 307.

tions at 150° and 200°C, when the minimum creep rate was of the order of 10^{-7} and 10^{-6} per hr, respectively. These are in good agreement with the authors' results. Crussard reported the equicohesion temperature to be dependent on strain rate within the range 150° to 200°C. Presumably, he did not extend his strain rates into the range where the authors found transition at higher temperatures. Regarding the temperature dependence of the minimum creep rate, he obtained a value for Q of 27,000 to 29,000 cal per g atom. The stress was not specified, but if we assume that it was the same as for the transitions he reported, i.e., about 2000 psi, fair agreement exists with the authors' value of about 31,000 cal per g atom (Fig. 20).

N. J. Grant (authors' reply)—The measure of the angle between the low temperature and the high temperature portions of the lines which are obtained from the plot of stress vs. rupture time or stress vs. minimum creep rate, is a questionable way of expressing the decrease of creep strength which occurs when the equicohesive range is crossed. In fact, this angle depends entirely on the type of coordinates and the scales used. Actually, if Mr. Roberts should plot the 900 F curves for 2S and 3S aluminum on linear coordinates, he would find that the decrease in rupture strength for 3S aluminum is very much sharper than for 2S aluminum.

The authors did not conduct creep tests over the entire range of temperatures with fine grained type purity aluminum because the fine grain size grows to a grain size of the same order of magnitude as the starting coarse grained specimens, when the test temperature was greater than about 700°F. These fine grained structures were completely unstable, the grain size growing at a very rapid rate due to the superimposed stress at temperature. Fine grained structures were therefore impossible to test because of this instability.

Fig. 22 is purely hypothetical and was not intended to be compared directly with the log-log experimental plots of stress vs. minimum creep rate. Fig. 22 simply justifies the existence of "breaks" in such plots in an indirect way. Primarily, Fig. 22 is intended to show that high purity materials give a wider range of temperature in which the grain boundary gradually contributes to the deformation process, whereas in commercially pure materials the grain boundary effect is quite sudden and sharper.

D. J. McAdam, Jr. (*Washington*)—This paper presents valuable information. However, the view expressed in conclusions 1, 2, and 3, that there is an abrupt "transition from low temperature to high temperature deformation," is not in accord with a large amount of evidence obtained by other investigators. Moreover, the authors' opinion that there is such a transition is based on an incorrect interpretation of the evidence in Figs. 3, 4, and 5. If the smooth curves drawn on the semilog scale in Fig. 3 were transferred to the log-log scale in Fig. 4, they would still be smooth curves, but with upward convexity. Moreover, smooth curves could be based directly on the plotted points in Figs. 4 and 5. I can see no justification for the straight lines used to represent the evidence in those figures.

The curvilinear relationship between stress and the creep rate would have been clearly revealed if the investigation had been broadened to include experiments at much lower strain rates. In the experiments represented in Figs. 4 and 5, the strain rates ranged as high as 1000 pct per hr, and the slowest strain rate was about 0.02 pct per hr. The lower the stress and the slower the strain rate, the more nearly does the creep approach truly viscous flow, in which the strain rate varies linearly with the stress. With approach to purely viscous creep, the slope of a curve on a log-log scale would approach a slope of 45°, if equally open scales were used for both stress and the strain rate. In Figs. 4 and 5 the relation between the scales of ordinates and abscissas is such that truly viscous flow would be represented by a line sloping at an angle of 63° 26' (tan^{-1} 2). To approximate viscous flow, the strain rates evidently would have to be much slower than those represented in Figs. 4 and 5, and the slopes of the curves would have to become much steeper.

A paper by Bennett and McAdam[1] describes an investigation of creep rates of Monel. As shown in log-log scale in Fig. 14 of that paper, the stresses ranged between 200 and 75,000 psi, and the creep rates ranged between 10 and 0.01 pct per hr. With decrease in the strain rate, the continuous curves approach a slope of 45°, thus indicating approach to purely viscous flow. This figure has been reproduced as Fig. 2 on p. 1031 of the 1948 *Metals Handbook* of the A.S.M. In a subsequent paper by McAdam, Geil, and Woodard,[2] the investigation of the same sample of Monel was extended to include experiments at still higher stresses, and the results are shown in Fig. 24 of that paper. Fig. 26 of the same paper shows a similar log-log relationship for oxygen-free copper.

Over a period of years, attempts have been made to express the relation between stress and the creep rate as a power function, represented by straight lines on a log-log scale. Other investigators have represented the relationship as an exponential function, indicated by straight lines on a semilog scale. In 1938 Nadai[3] pointed out the limitation of each of these methods of representation and suggested the use of a hyperbolic sine relationship. This relationship was discussed further in papers by Nadai and McVetty[4] and McVetty.[5] According to this relationship the minimum rate is proportional to the hyperbolic sine of the stress. At low stresses, this relationship corresponds approximately to purely viscous flow; at high stresses, it approximates an exponential relationship. The hyperbolic sine relationship can thus be represented by continuous curves for wider ranges of stress and creep rate than those used in most investigations.

N. J. Grant—We wish to thank Dr. McAdam for his discussion. It is very important to point out that our conclusions in items 1, 2, and 3 do not mention or even suggest "abrupt" transitions. Our position in this respect is clear and has been expressed previously (refs. 9 and 12) wherein it was explicitly stated that the "break" formed by two straight lines is a plotting convenience which shows the stress-temperature-rupture life or minimum creep rate relationships which contribute to the first evidence of grain boundary slip and fracture. Metallographic evidence of this is abundant and the results have been noted and reported innumerable times by White, Clark and coworkers, Parker, Thieleman, and many others.

In ref. 9 strain rates go to higher and lower values than shown in this report, the lowest values being of the order of 0.001 pct per hr. The total range covered was over seven logarithmic cycles. Straight lines were entirely applicable and did not suggest that a 45° slope was even to be approached. The idea of a 45° slope due to viscous flow is an entirely new idea, unproved and unsupported for metallic creep. Since the results of Bennett and McAdam[1] were based on creep tests which lasted only up to about 1000 hr, it was entirely unlikely that "minimum" creep rates were approached at all. At the low stresses used and for these short times, the rates are very probably off by a factor of 100 from the true minimum.

[1] J. A. Bennett and D. J. McAdam, Jr., "Creep Rates of Cold-Drawn Nickel-Copper Alloy (Monel Metal)," *Journal of Research, National Bur. Standards* (1942) **28**, pp. 417-437.

[2] D. J. McAdam, Jr., G. W. Geil, and D. H. Woodard, "Influence of Strain Rate and Temperature on the Mechanical Properties of Monel Metal and Copper," *Proc.* A.S.T.M. (1946) **28**, pp. 417-437.

[3] A. Nadai, "The Influence of Time upon Creep. The Hyperbolic Sine Law," Stephen Timoshenko Sixtieth Anniversary Volume (1938) New York, Macmillan Co.

[4] A. Nadai and P. G. McVetty, *Proc.* A.S.T.M. (1943) **43**, p. 749.

[5] P. G. McVetty, "Creep of Metals at Elevated Temperatures—The Hyperbolic Sine Relation between Stress and Creep Rate," *Trans. Amer. Soc. Mech. Engrs.* (1943) **65**, No. 7, p. 761.

DISCUSSION, B. Lustman presiding

P. H. Morton (*Metals Research Laboratory, Case Institute of Technology, Cleveland*)—I should like to ask the authors if they can give us any further information concerning the method of preparation of the titanium used in their investigation, as it appears to have an important effect on the properties. I have recently been working at Case Institute of Technology on the oxidation of titanium in the temperature range 600° to 1100°C. We used titanium sheet obtained from three different sources. Two of these had been melted during fabrication, whereas the third had been prepared by powder metallurgical methods. The latter behaved in a manner entirely different from the other two, but these two also showed significant differences in behavior. I should say that our work was done using an atmosphere of air rather than pure oxygen, and it may be that nitrogen was playing some part in the reactions. This could explain some of the differences between our results and those of the authors.

The method we used was a continuous, or rather semicontinuous one, whereby the scale was weighed as it formed. In most cases we found the scaling obeyed a parabolic law over considerable intervals of time, but as time increased at a fixed temperature, deviations were often observed. These deviations took the form of irregular increases in weight, which did not appear to be reproducible from one run to another. Sometimes the increase was sudden and sometimes more gradual, but the general weight increase was more rapid than it would have been if it had continued according to a parabolic law. I wonder if by taking discontinuous readings such as the authors', one could not in effect be smoothing out these irregularities and obtaining, as it were, an average of many runs and thereby obtaining a curve that appears linear.

Another interesting thing that we observed was a black coloration on the inside of the outermost rutile scale, which formed on many specimens scaled for long times. The outer scale, which could be stripped off easily by hand, consisted then of a single layer, the outside of which was yellowish and the inside of which was black. (This appearance of black coloring was in addition to, but distinct from, the same change from yellow to orange or brown as observed by the authors above 820°C.) This black material showed under X-ray exactly the same structure of rutile as the rest of the outer scale and showed no evidence of the deficiency of oxygen found by Ehrlich. However approximate electrical conductivity measurements at room temperature showed it to have a conductivity greater than that of the yellow scale by a factor of several thousand. We believe that it is probably the appearance of this black coloration and the concomitant increase in conductivity that explains the irregular increases in scaling rate that we observed. I would like to know if the authors observed any such coloration of the scales formed on the material used by them.

With regard to the lower oxides present, we found evidence of the TiO phase after cooling to room temperature. This was observed on the surface of the remaining metal, and had itself a metallic appearance. The structure revealed by X-ray was of the NaCl type, but with a parameter slightly greater than that reported by Ehrlich. Some confusion exists in the literature, but it is possible that this phase contained some nitrogen, or was composed in part of TiN. Both the monoxide and the nitride have the NaCl structure, but the effect of temperature and composition on the lattice parameter is not known to any great extent.

J. T. Waber (*Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico*)—The authors are to be complimented on continuing their good work in this difficult field. Their experimental conditions seem excellent. We must now add a linear growth law to those already observed for titanium, namely parabolic by Gulbransen and Andrew[1] and logarithmic by Alexander and Pidgeon.[2] Certainly above 820°C the growth appears to be linear.

This behavior of titanium thus is similar to that of aluminum, namely, that a logarithmic growth law obtains at low temperatures,[2] then changes to a parabolic and finally a linear one as the temperature is increased.[1]

It certainly appears from the data of Fig. 2 that a parabolic growth law is a better fit than the proposed linear one. Did the authors attempt to establish a parabolic law at the lower temperatures? It should also be pointed out that the discrete change of activation energy indicated in Fig. 3 might be attributed to a change in mechanism in the vicinity of 820°C.

The authors indicate that the rate-controlling step occurs at the oxide-gas interface and employ the "large" pressure dependence observed by Gulbransen and Andrew[1] to substantiate their claim. Waber[3] indicated

[1] N. F. Cabrera, *Revue Metallurgie* (1948) 45, p. 86.
[2] J. T. Waber, Discussion of ref. 2.

that the rate depended on the 0.33 power of the oxygen pressure instead of 1.0 power, as would be suggested by a gas-interface-controlled reaction. Furthermore, the high values of ΔE suggest that the reaction may be controlled by some diffusion process. I would certainly welcome a mechanism which would explain these facts and the linear reaction law from the viewpoint other than the usual one involving a porous oxide film.

In some preliminary experiments, we noticed a weight decrease while oxide layers were growing in thickness, as evidenced by interference colors. For this and other reasons, it appeared that hydrogen could escape through the oxide film. It would appear that if hydrogen did escape during the authors' experiments, the initial deviation would be even larger.

R. I. Jaffee (*Battelle Memorial Institute, Columbus, Ohio*)—Up to the present there has been speculation that titanium oxidizes faster in its β form than in its α form. This means that the curve of reaction rate vs. temperature should show a discontinuity upward at the transition temperature. It is somewhat discouraging, then, that the first investigators to present data confirming this point do not draw this conclusion.

Apparently the authors believe that the transformation had nothing to do with the observed discontinuity, because they state: "With normal impurities in Kroll titanium, the transformation occurs over the range 860° to 970°C." Also, they state that: "Any tendency toward lower transformation due to impurities should be counteracted by the oxygen dissolved in the metal." Both of these statements are clearly incorrect. The chief α-stabilizing impurity in Kroll titanium is iron, and it serves to lower the boundary between the α and the α plus β fields. The chief α-stabilizing impurities in Kroll titanium are oxygen, nitrogen, and carbon, and they serve to raise the boundaries between the β and the α plus β fields. Present together, the α and β stabilizing impurities do not offset each other. The more of each that is present, the higher is the upper transformation temperature and the lower is the lower transformation temperature.

Kroll titanium often contains sufficient iron as an impurity that a small amount of β phase is retained at room temperature, appearing as rounded islands in a matrix of α phase. What then is the lower transformation temperature? Clearly, there is none. Depending on the iron and other β-stabilizing impurity content, the lower transformation temperature can vary from 882°C down to room temperature and below. The lower transformation temperature given by the authors, 860°C, is somewhat high for normal iron-content impurity in Kroll titanium. The temperature of the discontinuity in the oxidation reaction rate, 830°C, is entirely reasonable as a lower transformation temperature for Kroll titanium. More important, it is a temperature at which one might reasonably expect appreciable quantities of α to start transforming to β phase.

Examination of a piece of Kroll titanium that has been oxidized above the upper transformation temperature will usually show an outer case of equiaxed α titanium and a core of transformed β titanium. This is caused by the concentration gradient of diffused oxygen from the surface inward, and the α-stabilizing nature of oxygen. The metal being oxidized under these conditions then consists of a case of α and a core of β titanium. If oxygen diffuses more rapidly in β titanium than in α, and, as a result, has a higher oxidation rate, then one would expect the diffusion of oxygen into a composite α case and β core to be more rapid than into an all-α body. Under these conditions the oxidation rate would be expected to be higher. It is suggested that this change of the titanium specimens, from structures that are all α below 830°C to composite α-β structures above 830°C, is responsible for the discontinuity in reaction rates.

M. Hansen *(Armour Research Foundation, Chicago)*—The authors have expressed the desirability of having available an accurate phase diagram of the Ti-O system before further work is warranted on the oxidation of titanium. For some time, an investigation of the constitution of the Ti-O system has been in progress in the Metals Research Department of Armour Research Foundation of Illinois Institute of Technology. Micrographic analysis, X-ray diffraction, and incipient melting studies are being used to determine the phase relationships. At this writing, the following main features of the system have been established:

1—The temperature of the $\alpha \rightarrow \beta$ transformation of titanium is raised to high temperatures by rather small additions of oxygen, resulting in a restricted field of β solid solution and an extended range of solid solution of oxygen in α titanium.

2—α solid solutions are stable to their melting temperatures, which are higher than the melting point of pure titanium.

3—In good agreement with Ehrlich's work, about 14 pct O (32 atomic pct) is soluble in α titanium at temperatures between 700° and 1500°C.

4—The TiO phase is stable within a wide range of composition, i.e., between approximately 20 and 30 pct O (42 and 55 atomic pct) at temperatures above 1200°C.

It is hoped that the final results of this investigation will be available in published form within the next year.

W. M. Fassell, Jr. and **W. McKewan** *(Dept. of Metallurgy, University of Utah, Salt Lake City)*—This paper is of particular interest to us because of our present work in progress on the high pressure oxidation rates of pure metals in dry oxygen. The most interesting feature of this paper is the fact that titanium shifts from parabolic to linear oxidation at approximately 650°C.

The authors are not quite correct in stating that no other cases, except aluminum, of this shift in oxidation type from parabolic to linear are known. Gulbransen[7] has shown that at temperatures below 450°C the oxide coating on magnesium is protective and nonprotective at 475°C and above. Leontis and Rhines[8] further investigated the linear oxidation of magnesium.

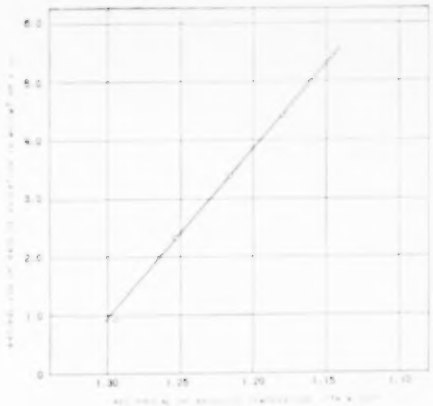


Fig. 4—Effect of temperature upon oxidation rates of tantalum

Research work in progress at the present time on tantalum indicates that above 500°C this metal also oxidizes according to the linear law, on the basis of preliminary data shown in Table II and Fig. 4, while at lower temperatures it apparently is parabolic. The activation energy E for tantalum in pure dry O_2 at 14.7 psi, according to the Arrhenius equation, $k = Ae^{-E/RT}$, is 57,800 cal and the action constant A is 7.0×10^{10} mg per sq cm per hr.

In the case of tantalum, the Pilling and Bedworth[9] ratio of volume of oxide to volume of metal is 2.33[9] and here one certainly would not expect the linear oxidation to occur on the basis of the Pilling and Bedworth criterion.

As more reliable data are being made available it appears highly questionable that the ratio of volumes of oxides to metals have much to do with the type of oxidation observed. In general, at least, it appears that if a metal forms only one predominant "stable" oxide (at any given temperature) it will shift from parabolic to linear oxidation at higher temperatures. This is true for Al-Al_2O_3, Mg-MgO, Ta-Ta_2O_5, and Ti-TiO systems.

We would like to ask the authors if they have observed an increase in the linear oxidation rate at constant temperature after long periods of oxidation. This phenomenon was observed by Leontis and Rhines[8] on magnesium, and on tantalum in the present investigation.

In the case of the discontinuity shown in Fig. 3, the possibility of anticipation of the transformation from hexagonal close-packed to body-centered cubic by the metal and/or oxide should not be overlooked. Since this transformation is the only known change occurring in the system in question in the temperature range of from 800° to 900°C, it may be in some way associated

Table II. Oxidation Rate of Tantalum in Oxygen

14.7 psi Absolute Oxygen Pressure
Preliminary Data

Sample No.	Temperature, °C	Rate, Mg per Sq Cm per Hr
A-14	500	0.252
A-13	525	1.607
A-12	550	3.86
A-11	575	8.4
A-4	600	22.9

[7] E. A. Gulbransen: *Trans. Electrochemical Soc.* (1945) **87**, pp. 589-599.

[8] Benjamin Lustman: *Metals Handbook*, p. 223 (1948); Cleveland A.S.M.

with up responsible for this discontinuity in oxidation rate.

M. H. Davies and **C. E. Birchenall** (authors' reply)—The authors are gratified at the high quality and quantity of discussion evoked by this paper. It is good to know that so much work is being done on this reaction and related subjects, for it is obvious that much remains to be done before a reasonably complete understanding of the mechanisms will be achieved.

Mr. Morton's remarks should leave no doubt that our results are not a satisfactory basis for predicting the behavior of titanium in air at high temperatures. Since the paper was written, one of us (M.H.D.) has run titanium samples in oxygen and air under conditions otherwise the same. Whereas only a very thin black discoloration was observed next to the metal with pure oxygen, oxidation in air produced considerable quantities of powdery black oxide of rutile structure between the metal and the compact orange-brown layer. It is evident that the presence of nitrogen influences the course of the reaction.

Measurements were made using both weighings before and after oxidation on separate samples and continuous runs on a spring balance as stated. No systematic differences were observed, nor was there any reason to believe that the curve was composed of "fits and starts."

The demonstration of a phase with a NaCl structure in the scale is very interesting to us. It is unfortunate that present X-ray techniques will not permit a determination among oxide, nitride, and mixed crystal containing both anions.

It should be worthwhile in connection with several discussions to state the analyses on the commercial titanium sheet used here. Carbon was obtained by combustion, nitrogen by the micro-Kjeldahl method, and all other elements by spectrograph. Oxygen analyses were not considered necessary because of the use to which the metal was put. Exclusive of oxygen, the material appears to be better than 99.5 pct Ti. The impurities are: 0.15 pct C, 0.004 N, 0.15 Mn, 0.08 Fe, 0.005 Al and Mg, < 0.003 Zr, 0.004 Si, 0.001 Mo, < 0.001 Ni, Cu, Pb, Cr, V, < 0.0005 Cu; did not detect Sn, Co, W, Hf, Au, As, Ta, Cb, B, P, Be, Ga, Cd, Y, Yb, In, Ir, As, Os, Lu, Na.

Attempts to fit the parabolic rate law at temperatures below 820 C leads to systematic deviations at long times. It is easier to find reasons for initial deviations which are often observed even when the long time data follow the parabolic equation. All deviations follow from a weight gain greater than the linear law indicates.

The reaction of oxide and gas at the common interface is not likely to be a simple process. If this should be the locus of the rate controlling step, it is still not certain what that step is. If it should be solution of oxide ions in the lattice, the pressure dependence might be the 0.5 power which may not be too far from the 0.33 power which Dr. Waber reports for the Gulbransen and Andrew measurements.

We have no evidence at all on the amount of hydrogen in the sample nor its mechanism and rate of escape. We would expect that its effects would be confined to the initial period.

We find it a little difficult to determine whether Dr. Jaffee argues that β titanium reacts to form oxide faster than α, yielding a higher true oxidation rate, or β permits oxygen to diffuse more rapidly in solid solution than α, thus giving a higher apparent rate of oxidation under the conditions of measurement. It seems to us that he takes care of the first possibility in his last paragraph where he cites the metallographic evidence that during oxidation of Kroll titanium above its upper transformation temperature the oxide scale is still directly in contact with α titanium due to the solution of oxygen, which stabilizes the α phase relative to β in spite of small quantities of other impurities. With regard to the solution of oxygen in a β core, it should be noted that, although the diffusion coefficient may be (and probably is) higher than in the α rim, the solubility of oxygen in β titanium is quite low compared with its solubility in α, so that the actual rate of diffusion, the quantity of oxygen transferred, may be little greater than in homogeneous α titanium. Admitting that it is desirable to separate the oxide formation rate from the oxygen solution rate, which we hope to do in time, we still feel that the weight of evidence does not favor the α-β transformation as the cause of the 830 C break, although future studies may reveal a way to assign the responsibility to that cause. The phase diagram information being obtained by Dr. Hansen and his coworkers should be of great assistance in future work.

The linear oxidation of magnesium has been shown by Leontis and Rhines to yield a powdery product contrary to the qualifications placed on our statement about the scale on titanium and apparently on aluminum. We have no information beyond 24 hr at 800 and 15 hr at 900 C. In that period we have observed no accelerated rates such as Leontis and Rhines found for magnesium and Fassell and McKewan report here for tantalum.

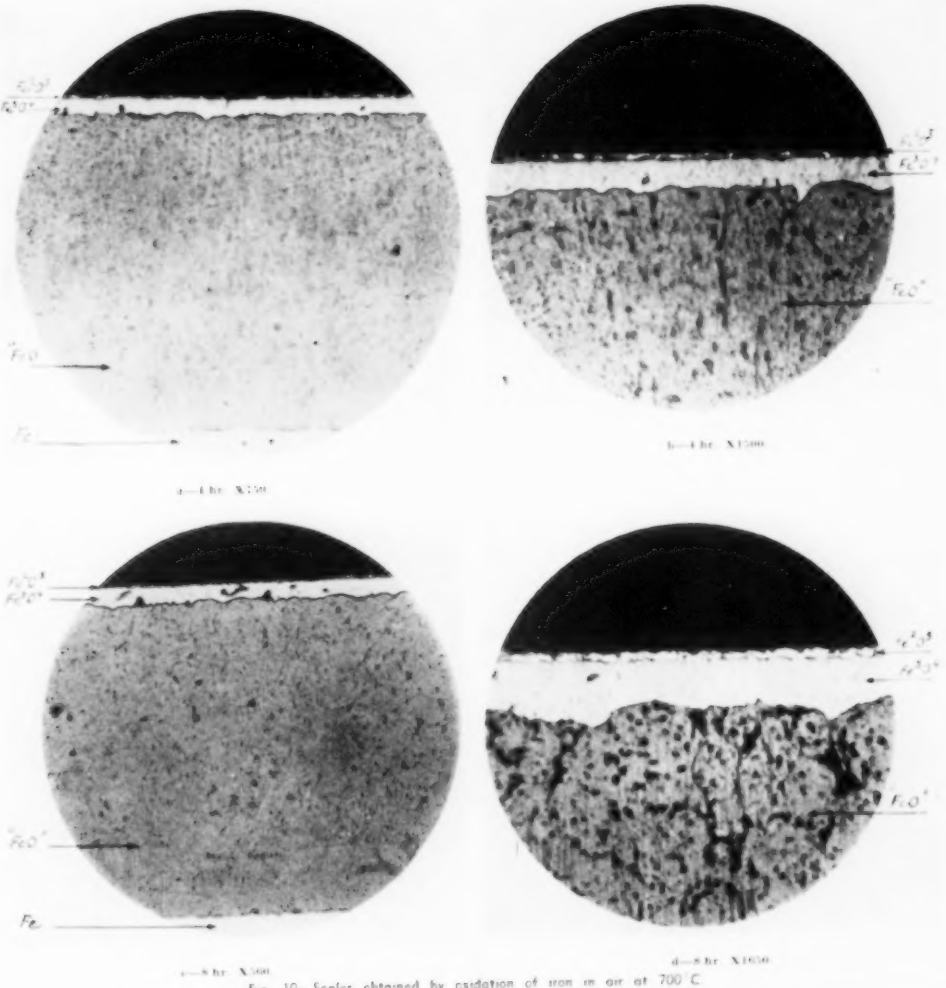
On the Mechanism and Kinetics of the Scaling of Iron

by C. Wagner and W. Hauffe

DISCUSSION, H. Uhlig presiding

P. Paidassi (Professor of Metallurgy, University of Coimbra, Chile)—It is stimulating to realize that the mechanism of the oxidation of iron at high temperatures has been increasingly occupying the attention of researchers in recent years. The way pointed out by the publications of Benard and coworkers (i.e., the separate study of the constitution and the rate of growth of each of the oxide layers forming the scale as the latter develops) has proved fruitful. We have the right to expect it to lead to a prompt and complete solution of this difficult problem. However, if the phenomenon of oxidation is already known in its outline, several points of detail are yet to be discussed and clarified.

This interesting paper throws no inconsiderable light on several of these points, particularly on the law of



a—4 hr, X500 b—4 hr, X1500

c—8 hr, X500 d—8 hr, X1650

Fig. 10—Scales obtained by oxidation of iron in air at 700°C.

growth of external layers (Fe_2O_3 and Fe_3O_4), their relative importance as a function of temperature, the part taken up by the diffusion of the Fe^{++} and O^{--} ions in the growth of each layer, etc. We hope to publish within a few months our results with regard to these problems, which we are investigating jointly with Professor Benard. Nevertheless, we should like to state from the outset our position regarding the first two points just referred to.

In the first place, we think we are justified in affirming that the scale formed over Armco iron, which has been oxidized in air from 700°C upward for oxidation times of not more than 1 hr, has an external layer of Fe_2O_3 oxide thick enough to be seen and measured micrographically. We insist on this point because we see from Table I that no mention is made of this layer over the whole temperature range of 600° to 800°C. In addition, in their discussion of the work of Stanley and coworkers,[7] the authors seemed to cast doubt on the fact that the phase of Fe_2O_3 could be visible at temperatures below 800°C. In support of our opinion we are presenting several micrographs (Fig. 10) which, although hastily prepared for the sake of the present discussion,* may perhaps be considered more convincing than those of Stanley and coworkers.

* We are constrained to reproduce our micrographs for 4 and 8 hr oxidation times, which show thick enough Fe_2O_3 scales, but our micrographs for 1 and 2 hr are scarcely less defined.

The fact that, like Benard and coworkers, Tesche, Stanley and coworkers, we have in these experiments operated in nondried air, does not seem to us to detract greatly from the value of these micrographs, since the presence of humidity in the oxidizing medium, as well as the diminished oxygen pressure, should normally stand in the way of the formation of this Fe_2O_3 layer (the authors themselves realize it as regards the first point). We are furthermore inclined to believe (without, however, having exhausted our study) that humidity within practical limits (air at 15° to 20°C with a variable relative humidity) and an oxidation temperature of 700° to 950°C have no appreciable influence over the growth rate and the thickness ratios of the different oxide layers. This opinion is borne out by the regularity of the results, presented later in this discussion, since they were obtained in spite of the variable relative humidity of the ambient

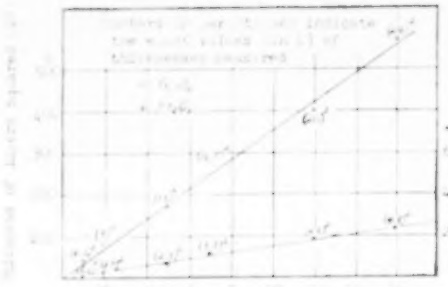


Fig. 11a—Curves for the growth of the layers Fe_3O_4 and FeO at the scale obtained by incomplete oxidation of iron in air at 850°C.

Fig. 11b—Variation as a function of oxidation time of the relative thickness of the Fe_3O_4 and FeO layers with regard to the total thickness of the scale on iron oxidized at 850°C.

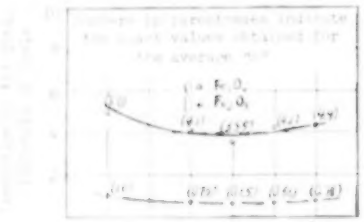


Fig. 12—Variation as a function of temperature of the relative thickness in pct of Fe_3O_4 and FeO oxide layers with regard to the total thickness of the scale.

Each experimental point corresponds to the average of that relative thickness—practically constant as regards variable oxidation times between 0 and 16 hr. Averages obtained analogous to Fig. 11b.

on. Neither do we think it necessary to take the analysis of the metal into account, since the Armco iron utilized showed a high degree of purity (over 99.92 pct total iron).

The reason that the authors did not observe the FeO phase might be found in their modus operandi, which, though very elegant, has a drawback (to judge from the description in the paper and from the discussion cited[1]), namely, that it leaves, at least for some instants, the oxidized sample in an atmosphere of argon at the temperature of the experiment. It is not impossible that because the supply of oxygen is cut off, the iron diffuses through the superior oxides quickly enough to alter their relative proportions, the thickness of the FeO thus diminishing to the extent of rendering the oxide no longer micrographically visible, or perhaps making it disappear altogether. In order to determine whether this hypothesis is in any way helpful, it would doubtless be sufficient if the authors tried cooling the sample as quickly as possible in an atmosphere of oxygen without the previous admission of argon.

This interpretation of the authors' results touching the range of temperature when the FeO phase is present in the oxidation scales is in line with the remarks of Gulbransen.[8,9] He established, for much thinner layers, the importance of the cooling medium for the phases observed, although as far as we can determine he has not explicitly stated the hypothesis that possibly the main reason for this change might be an appreciable rate of diffusion of iron through the higher oxides. Should the responsibility lie with the technique of the authors cited, their conclusions regarding the percentage of higher oxide layers in relation to wüstite and their law of growth would be less convincing. It is apparent from the dispersion of their results touching these points (Table I) that the authors have endeavored to establish these laws in an indirect form—oxidation of "FeO" and Fe_3O_4 by means of oxygen. It seems to us, however, that just because the curves showing the increase in weight of "FeO" and Fe_3O_4 layers by oxidation are parabolic (for the oxidation of magnetite at 850°C the deviation from the parabolic law does not seem to be negligible), this does not necessarily imply that the laws of growth of Fe_3O_4 and FeO, on their substrate of FeO in the presence of an excess of as yet unoxidized iron shall likewise be parabolic. (There could be effects both of the gradient of iron concentration on wüstite and of the possible presence of cracks in the wüstite or magnetite samples utilized resulting from the method of preparation.)

We have preferred to attempt to perfect our micrographic technique with a view toward obtaining direct proof, in spite of the difficulty involved. We have thus been able to establish that these laws are parabolic for the temperature range of 700° to 950°C.[10] By way of example we have prepared growth curves of the three oxides, FeO, Fe_3O_4, and Fe_2O_3, on Armco iron oxidized in ambient air at 850°C. (The previous treatment had been polishing with metallographic paper to a fineness of 3/0, followed by hydrogen annealing at 950°C for 3 hr.) In spite of the relatively small thicknesses measured, it is possible to ascertain that the parabolic law is verified with a satisfactory precision. Fig. 11a. Fig. 11b shows the percentages of the thicknesses of the higher oxides to the total thickness of the scale with regard to oxidation times. These percentages remain constant within a tolerable range of dispersion. Fig. 12 shows the variation of the preceding average percentages with regard to the oxidation temperatures ranging from 700° to 950°C.[†] This diagram completes a part of the well-known diagram of Benard and Coquelle,[7] since on the one hand it is established as valid in this temperature range for any oxidation time exceeding 1 hr, and since on the other hand it fixes the proportion of the Fe_3O_4 phase in relation to the accompanying ones. In addition, it enables us to ascertain that the percentages referred to remain practically constant as a function of temperature, which permits certain consequences to be inferred regarding the range of stability of the Fe_3O_4 and Fe_2O_3

[8] E. A. Gulbransen: Progrès dans l'étude de l'oxydation superficielle des métaux et alliages a des températures élevées, Revue Métallurgie (July 1948) pp. 292-293.

[9] Discussion on "An X-Ray Study of the Scale Formed on Iron Between 400° and 750°C," by O. A. Tesche. Trans. A.S.M. (1950) 37, pp. 840-849.

[10] J. Pontnau: Contribución al estudio del mecanismo de la oxidación del hierro puro. Paper read at the Fifth South American Congress of Chemistry, Lima, Peru (May 8-13, 1951).

[†] The points corresponding to 850°C need great confirmation owing to the fact that at the time this work was completed we had only thin Armco sheets, which forced us to limit the oxidation time for this temperature to 15, 30, and 45 min. However, such a result, although provisional, shows that we did not find any discontinuity at the 850°C transformation temperatures for the Fe_3O_4 transformation, which is in agreement with the result obtained by the authors.

solid solutions and permits fixing the limits of these ranges as a function of those of wüstite.

The curves in Figs. 11 and 12 correspond to the fundamental phenomenon of the oxidation of iron, which in the pure state must be considered a phenomenon of diffusion without the limiting intervention of interfacial reactions. However, these curves may be considerably modified by numerous factors which may be termed complementary. For example, the rate of cooling or the cooling medium after the oxidation experiment may, without the authors' knowledge, have influenced some of their results. Other factors such as the cracking of the scales or their peeling from the substrate of iron must have been relegated to the background by the authors' technique, which probably permits the relative surface of peeling to diminish considerably, particularly at temperatures above 900°C.

We are at present engaged in the study of some of these factors we call complementary, with the object of being able at some future time—certain restrictive conditions being fulfilled—to establish the sample's history in the course of its oxidation by a simple micrographic examination. Fig. 13 shows the external part of an oxidation scale (800°C, oxidation time of 12 hr) and provides a good instance of cracking in an Fe_2O_3 layer. The cracking is brought about in the course of oxidation while the Fe_3O_4 phase penetrates along the cracks. We are presenting it in this discussion because it has the advantage of showing with great clarity allomorphous particles of Fe_3O_4 precipitated in the course of the oxidation in zones where the wüstite, in our opinion, presents an increased porosity. The authors observed similar phenomena while working with Puron iron. (Stanley and coworkers did not observe this precipitation of Fe_3O_4 and suggested as a possible explanation the purity of the metal employed, although we ascertained that the reagent used by them was not the most adequate to make this type of precipitation evident.)

Finally we should like to congratulate the authors on the ingeniousness of their apparatus. In this connection, we would like to have the name of the maker of the "Nispan C" alloy utilized, as well as the characteristics of their spring set-up, and the approximate length necessary for the glass head (for instance the vertical distance between the connections *A* and *I* of Fig. 9) to permit the use of the spring suspension. Such an adaptation of the McBain balance will certainly prove very useful for the study of certain oxidation problems in controlled atmospheres.

A. deS. Brasunas (*Oak Ridge National Laboratory, Oak Ridge, Tenn.*)—The fact that the authors did not observe any discontinuities at transformation temperatures in plotting the rate constants against $1/T$ is not at all surprising. Other investigators[7, 8] who have observed these discontinuities have confined their attentions to thin films where the nature of the metal substrate can exert a measurable effect on the oxidation rate. It is very unlikely that such effects can be detected by measuring oxidation rates based on thick oxide layers, such as the authors have encountered.

Very recent work which the present writer has undertaken[9] agrees with the authors' findings that inert markers at the original iron-atmosphere interface do not move. However, we found ample evidence of oxide ion migration inward beneath the inert marker, which must necessarily occur to maintain contact between the growing oxide layer and the receding metal interface.

M. H. Davies, M. T. Simnad, and **C. E. Birchenall** (authors' reply)—We are extremely pleased to see the report which Professor Paidassi gives of his excellent work on the scaling of iron. Despite minor differences on a few points, the major discrepancies between our results and those previously obtained by metallographic means seem to have been resolved. Thus parabolic growth of Fe_3O_4 and Fe_2O_3 is established, and the sharp increase in the fraction of the scale occupied by these phases above 910°C is eliminated.

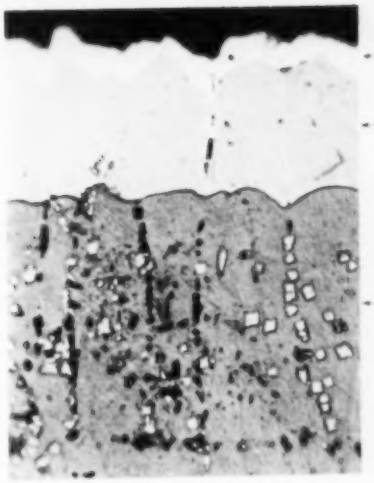


Fig. 13—Oxide layers formed on iron at 800°C, 12 hr. X1500.

We do not doubt that the Fe_3O_4 thickness measurements at 700°C are correct. Our failure to resolve this phase below 800°C is probably related to metallographic technique rather than the cooling of our specimens. These specimens were moved to the cold end of the furnace immediately at the end of the run. They were not in the hot zone of the furnace in the absence of oxygen long enough for layers of the thickness shown here to be reduced by the diffusion processes known to occur in Fe_3O_4.

Since the growth of each of the oxide phases is diffusion-controlled, we continue to believe that the growth of Fe_3O_4 on Fe_2O_3 is the same process regardless of whether wüstite and iron lie on the other side of the Fe_2O_3 or not. The only difference is probably the fact that Fe_2O_3 is growing also in the former case but not in the latter. Thus the rate constants obtained in the two cases must be compared through some analysis such as that of Valensi rather than directly.[4]

It is evident, particularly in Fig. 13, that surface roughness may play an important role in determining the initial rates, so that the deviations from the simple parabolic law in Fig. 7, for Fe_2O_3 growing on Fe_3O_4 at 550°C, are to be expected by the weight-gain method. Direct thickness measurement is undoubtedly less sensitive to this source of error, though not always completely free of it.

Metallographic studies in this laboratory by Himmel on the decomposition of wüstite on cooling indicate quite conclusively that the little cubes of Fe_3O_4 observed in Fig. 13 are due to simple precipitation when wüstite of oxygen content greater than eutectoid composition is cooled into the wüstite plus hematite region of the phase diagram. The specimens could not be quenched rapidly enough to prevent this reaction, although the eutectoid decomposition was easily avoided. Hence, these are not in themselves evidence for porosity.

It is not clear how the solubility limits for Fe_3O_4 and Fe_2O_3 can be fixed from the measurements of oxidation kinetics without knowledge of the mobilities of the ions in these phases or without some sort of chemical analyses. Himmel and Birchenall have measured

[7] G. Tammann and G. Siebel: *Ztschr. anorg. allgem. Chem.*, 1923, 148, p. 297.
[8] A. Portevin, E. Prétet, and H. Jolivet: *Revue Métallurgie*, 1931, 28, p. 221.
[9] H. Uhlig and A. deS. Brasunas: *Trans. Electrochem. Soc.*, 1950, 97, p. 440.

the iron ion mobilities in these oxides by following the diffusion of radioactive Fe.

The Norpan C wire used in these experiments was provided us by W. A. Mudge of the International Nickel Co. Professor Parlee can obtain information about this material by writing to that company. The springs may be wound with the wire in soft condition, then heat treated to improve the elastic properties.

We need only refer Dr. Brasunas to the work of Frechheck and Salzer[7] to indicate that discontinuities in the rate constant-temperature relation have been reported and attributed to the $\alpha \rightleftarrows \gamma$ iron transformation. The necessity for oxide ion diffusion in the absence of marker movement is not made clear by the two sentences devoted to that subject. Experimental uncertainty in the location of the marker will always allow for some oxide ion diffusion. Its magnitude can probably be determined best by direct measurement of oxygen diffusion in wüstite.

Role of Gases in the Production of High Density Powder Compacts

DISCUSSION, V. Pulsifer presiding

H. S. Kalish (*Sylvania Electric Products, Inc., Bayside, N. Y.*)—The authors' techniques of using permeability measurements to supplement density measurements in deducing sintering progress was well done. In addition they have clearly shown the necessity for removing the gas which results from the reduction of the oxides before the sintering process goes too far and how this gas can hinder sintering. They neglected to give sufficient importance, however, to the necessity for this reduction in the sintering process.

The portion of the article on the "Effect of Sintering at 1400° C in Hydrogen and Helium on Compacts Pressed at 50 tsi" is somewhat confusing. It is stated here that the expansion of pores, or better the retarding of sintering by pore gases, could be due to the reduction of oxides by hydrogen or carbon, or due to the liberation of adsorbed gases.

It is well known that hydrogen will reduce either iron or cobalt oxides at these temperatures, viz., 1400° C. If this is so, there is more reason to expect that sintering in hydrogen should give a lower density and a higher permeability. The hydrogen sintering is, however, outstandingly superior in producing a more dense sintered product. This I have observed frequently in working with stainless steel powders. You cannot sinter these compacts in the purest helium or in the best vacuum and get good density. It is essential that pure dry hydrogen be used to reduce the oxides present in these compacts. When the reduction is complete a good clean oxide free surface results and then the particles can sinter together. The authors have shown that this reduction must be completed before sintering progresses too far, but they gave no emphasis to the necessity of the hydrogen for this reduction. Although a large percentage of the oxide can be removed by decomposition in helium or in vacuum it cannot be removed as completely or as readily as when it is hydrogen-reduced. In addition the oxide which remains is at the outside of the particle or in the pore—just where it will hinder sintering. I sintered some stainless steel powder in a vacuum of about 10^{-5} mm and got a good deal of the chromium oxide to come out. It may not have even decomposed but just had a high enough vapor pressure to get pumped out. Much of the oxide remained on the compact, however, and it was clear that the vacuum sintering was not feasible.

I made a very close examination of the micrographs in this paper and even drew a few lines through them to see how true a representation of the actual porosity they were. I found them to be very good indeed. Ordinarily you can find a very distinct directional effect which shows up the polishing direction. These were a very good representation of the true porosity, however, so good that Table VI was prepared to show them.

In general, micrographs show a higher porosity than that which really exists because the pores are always enlarged a little during even the most careful metallographic preparation. These were so good, however, that a certain trend seems to exist. In the pressed compact we have a mixture of cobalt and iron. In the early stages of sintering the cobalt and iron, per se, remain and little alloying occurs. With more sintering we get more diffusion and more alloying. Thus the density calculated on the basis of a mixture is closest to the measured one until densification, diffusion, and alloying have gone a long way. Only the last two calculated densities based on the alloy density, therefore, are closest to the measured values, since the alloy seems to have a lower density than that indicated by the rule of mixture.

D. Warren and **J. F. Libsch** (*authors' reply*)—The authors wish to thank Mr. Kalish for his discussion of the paper and are particularly appreciative of his measurements of the porosity present in the powder compacts from their micrographs. It was interesting to see how the compact density calculated on the basis of the ideal density and on the basis of the mixture density compared with the measured density at the two extreme stages of the sintering process.

With regard to the comments concerning the reduction of oxides by hydrogen during sintering, the authors regret not having emphasized that the experiments designed to allow for the removal of gases from the compacts by variations in the sintering cycle were all conducted in a hydrogen atmosphere. In fact, all compacts, except where otherwise noted, were sintered in pure dry hydrogen. The purpose of the helium-sintering experiments was to study the process of gas evolution and pore expansion in the absence of a reducing atmosphere (hydrogen). It was not intended to suggest that sintering in helium was superior to that in hydrogen, but only to show that gas evolution could proceed by thermal decomposition of oxides or by reduction of oxides with carbon.

Table VI. Porosity after Various Sintering Treatments

Fig. No.	Compacting Pressure, tsi	Sintering Temperature, °C	Sintering Time, hr	Pct Found in Micrographs	Density Calculated from Pct Based on Reported Ideal Density of 8.80g per C u C m	Based on Mixture Density of 8.80g per C u C m	Reported by Author: Gper C u C m
14	50	1400	0.5	12.4	8.76	8.96	8.30
15	50	1400	4	10.5	8.79	8.71	8.45
12	50	1400	0.5	14.0	8.87	8.55	8.60
9	25	1400	1	10.5	8.58	8.40	8.60
18	50	1400	0.5	7.0	8.58	8.81	8.75
20	25	1400	24	04.4	7.92	7.98	7.90
21	25	1400	24	06.1	7.70	8.04	7.90

* Referred to helium. Others referred to H.

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aime NEWS

Reinartz To Head Slate Of 1953 Nominations

The Nominating Committee for Institute Officers in 1953, John R. Suman, chairman, completed its work at the Annual Meeting in February, and has made its report to the Board of Directors. The President-Elect in 1953 serves as President in 1954. The ticket follows: For President-Elect and Director, Leo F. Reinartz; for Vice-President and Director, A. B. Kinzel and Lloyd E. Elkins; for Director, Hjalmar W. Johnson, Philip Kraft, Gail Moulton, Edwin L. Oliver, Philip Wilson, and Elmer Isern.

Mr. Reinartz is a vice-president of the Armco Steel Corp., Middletown, Ohio.

As required by the bylaws, brief biographical sketches of the nominees will be published in the July issues of the journals.

Bowman, NAM, To Speak At Iron & Steel Dinner

The regular annual May dinner of the Iron and Steel Div. of AIME will be held May 21 at 7:00 pm at the Engineers' Club, 32 W. 40th St., New York, the evening preceding the banquet of the American Iron & Steel Institute. Chairman K. C. McCutcheon has obtained Dr. Neal Bowman, staff speaker for the National Assn. of Manufacturers, as speaker of the evening. His subject will be *Selling America—Your Job.*

NEAL BOWMAN

All AIME members and guests (stag) are welcome. The price of the dinner will be $6.00 and a cocktail bar will be open on the 10th floor of the Engineers' Club from 6 pm. For reservations write E. O. Kirkendall, Secretary, Iron and Steel Div., AIME, 29 W. 39th St., New York 18, indicating the number of reservations desired.

Dr. Bowman was professor of marketing in the school of business and public administration at Temple University for 17 years. He has written several books on advertising and selling and recently published a book on the principles and practices of public speaking.

Return Cards Promptly For New Directory Listing

Last month, reply postal cards were sent to all AIME members asking for information for listing their names in the 1952 Directory, to be issued late in the year. Members are urged to return the cards as promptly as possible, with information as to their company connection and address. If cards are not returned the address to which the cards are mailed, and which is given in the upper right-hand corner of the reply card, will be used in the Directory. This is the address to which we are now sending AIME publications. In many instances it is the home address of members, whereas the address and position given in the Directory is customarily the company or office address. All records are being transferred to the Flexoprint system, which takes some months to complete. When completed, a Directory can be printed on short notice at any time. The geographical section of the Directory will revert to the straight geographical arrangement, by countries, states and provinces, and towns, as used in the 1948 and preceding Directories. The geographical listing of members' names will include for the first time the major Divisional interest of each member as well as the Divisions in which he is enrolled, which information is given on the stencil but is not required on the return card. The Directory will be mailed only to those who make the appropriate check on the return card; it will be supplied to any member in good standing free of charge on request.

If you have not returned the card, do so now. If, by chance, you did not receive one, please write and ask for one. Advise headquarters immediately if you change your position or address, giving both the address you wish used for publications (if it is being changed) and the listing you wish in the Directory.

J. L. Bonanno Addresses Powder Metallurgy Group

A record attendance of 81 was recorded at the Mar. 19, 1952 meeting of powder metallurgists at the Brass Rail in New York. Chairman R. P. Seelig, vice-president, American Electro Metal Corp., introduced Joseph L. Bonanno, chief engineer, Lionel Corp., Irvington, N. J., who spoke on *In-Plant Production of Powder Metallurgy Parts.*

Mr. Bonanno discussed the roles of the custom fabricators and in-plant producers of parts, and explained the procedures and methods used by the in-plant producer. Most companies using powder metal parts in their products, usually have the parts made by a custom fabricator. However, when the volume of parts becomes very large, plants turn to internal production. In order to make in-plant production pay, there must be a peak production load, and continuous operation. Any overload would be turned over to a custom fabricator. The plant must have good machine shop and maintenance facilities, and a laboratory for preliminary studies, control, and evaluation.

Annual Meeting Paper Deadline

Sept. 15, 1952 is the deadline for all Institute of Metals Div. papers for the 1953 Los Angeles Annual Meeting and the deadline for all Iron and Steel Div. and Extractive Metallurgy Div. papers to be prepublished.

For the Annual Fellowship Dinner, the Ballroom was completely filled, and an adjacent room opened to handle the overflow. Committee officers and guests are shown at the head table just before dinner was served.

Delegates to Iron & Steel Technical Sessions Set New Attendance Record

Approximately 1660 Convene in Pittsburgh, Next Blast Furnace And Open Hearth Conference to Be Held in Buffalo, Apr. 20 to 22, 1953

THE Blast Furnace, Coke Oven and Raw Materials Committee and the National Open Hearth Steel Committee ran well in front of the conferences held at the William Penn Hotel, Pittsburgh, Mar. 31 to Apr. 2, 1952. The high quality of the papers presented, and the lively discussion drew a record crowd of iron and steel operators, superintendents and metallurgists. Registration for the Blast Furnace, Coke Oven and Raw Materials Sessions was approximately 420, and that for the Open Hearth Steel Conference was 1240. Many companies are taking even greater advantage of the opportunity to have their men attend the conferences and discuss mutual problems with other engineers from all parts of the country.

All technical sessions were well attended, some sessions had standing room only. With the present requirements of producing more steel more economically, all information presented is thoroughly considered. It has been said by many conference attendees, that if they acquire but one idea, or even a germ of an idea, the company expense in sending them is more than repaid.

The annual luncheon and business meeting of the Blast Furnace, Coke Oven and Raw Materials Committee was held on Tuesday April 1, with Chairman E. K. Miller presiding. He introduced several of the committee members, and Open Hearth Chairman Al Sommer. The most interesting and outstanding of the committee reports given was the news that the committee has turned its debit of last year into a respectable bank balance. The Institute was well represented at the luncheon with the welcome appearance of Mike Haider, AIME President, and Past President L. E. Young, a familiar figure in the Pittsburgh area. President Haider said that he was impressed with the large conference attendance.

So great was the demand for tickets to the Annual Fellowship Dinner on Tuesday evening, that many people found themselves seated in the balcony of the Ballroom, and a large group was placed in an adjacent room. Music was provided by the Homestead District Works Male Chorus of U. S. Steel Co.

Open Hearth Chairman Al Sommer, after welcoming the group, introduced Blast Furnace, Coke Oven and Raw Materials Chairman E. K. Miller. Mr. Miller in turn introduced Samuel Naismith, who will assume the Chairmanship of the latter committee. Al Sommer then presented the past chairman's certificate and perpetual registration to H. M. Griffith. Electric clocks were then presented to all past chairmen of the National Open Hearth Committee; H. M. Griffith, E. G. Hill, C. R. Fondersmith, W. C. Kitto, E. L. Ramsey, A. P. Miller, and L. F. Reinartz. The clocks were inscribed *Presented to — In appreciation for long and conscientious service.* J. J. Golden was

General Richie D. Somervell, chairman of the board, Koppers Co., served as Toastmaster at the Annual Fellowship Dinner.

H. M. Griffith receives from Al Sommer one of the clocks awarded to all Past Chairmen of the National Open Hearth Committee.

Speaker Steve M. Jenks, Vice-president manufacturing, U. S. Steel Co., discussed steel industry achievements.

Homestead District Works Male Chorus of U. S. Steel Co. provided several vocal renditions at the dinner.

Al Sommer presented the McKune Award to J. M. Kelly and V. H. Bridgewood for their excellent paper on "Charge Control for a Basic Open Hearth Furnace."

introduced as incoming Chairman of the National Open Hearth Committee.

The McKune Award was presented to J. M. Kelly and V. H. Bridgewood, Steel Co. of Canada. Richard D. Bubdy, Wheeling Steel Corp. received the Conference Award.

Gen. Brehon D' Somervell, Toastmaster, called upon AIME President Haider, who pointed out the active part the Iron & Steel Div. was playing in Institute affairs. President Haider also announced that Leo Reinartz had been nominated as President-Elect for 1953, which would mean the 1954 AIME Presidency.

Gen. Somervell then ably introduced Steve M. Jenks, U. S. Steel Co., Speaker for the dinner. Mr. Jenks discussed development and achievements of the steel industry.

On Wednesday, the U. S. Steel Co. played host to the registrants, conducting an all-day plant visit, including a luncheon. A special train carried the group to the Homestead district works, and those primarily interested in blast furnaces were taken to the Carrie furnaces. At Homestead, the tour was conducted through the 45-in. slabbing mill, and open hearth shop No. 5. Many of the visitors stopped to compare notes and talk shop with the operators in charge. The group then entrained for Irvin works, where huge tents were set up as a restaurant. The delicious dinner and the opportunity to rest weary feet were appreciated. The tour through Irvin works included the hot and cold rolled strip mills, galvanizing line, and the hot-dip and electrolytic tin lines.

It cannot be said that the conference was all work and no play for the registrants. The numerous suppliers present provided handsomely for the leisure hours, and cooperated with the conference committees by remaining inactive during the technical sessions.

Incoming officers for the Blast Furnace, Coke Oven and Raw Materials Committee are: Samuel Naismith, Chairman; C. C. Russell, Vice-Chairman; Kurt Neustaetter, Vice-Chairman; and R. E. Powers, Secretary. National Open Hearth Steel Committee officers are: J. J. Golden, Chairman; A. H. Sommer, Past Chairman; L. R. Berner, Vice-Chairman; and Ernest Kirkendall, Secretary.

Leo Reinartz, nominated as AIME President Elect for 1953, accepts his gift as a Past Chairman of the National Open Hearth Committee.

J. J. Golden, who will take over the reins as incoming National Open Hearth Chairman, addressed the group.

AIME President Mike Haider pointed out the active part the Iron & Steel Div. plays in Institute affairs.

Blast Furnace, Coke Oven and Raw Materials Committee Chairman E. K. Miller introduced incoming chairman S. Naismith.

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Included in this volume are chapters on elementary rolling theory, evaluation of hot malleability of Ni and high Ni alloys, and rolling Ni and high Ni alloys, Cu and Cu alloys, Zn, Al alloys, Mg base alloys, and some precious metals.

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The volume contains an appraisal of wire products, and production data on high C steel wire, stainless rods and wire, Monel rods and wire, Cu and Cu alloys, Al and Al alloys, and Mg alloys.

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Miro Mihelich has been appointed manager of Harbison-Walker Minerals, Ltd., a subsidiary company of Harbison-Walker Refractories Co., organized for developing sources of raw materials in Brazil.

MIRO MIHELICH

B. Dean Bowen is now junior engineer with Hotpoint, Inc., Chicago.

H. W. Rathmann, Vanadium Corp. of America, Bridgeville, Pa. is now development metallurgist at Niagara Falls, N. Y.

Satyabrata Sarkar has joined the Metal Corp. of India Ltd., Katras-garh, India.

Stanley Hale is plant superintendent of Federated Metals Canada Ltd., Toronto. The firm has been formed by the American Smelting & Refining Co., New York, and the Frankel Corp., Ltd., Toronto to handle the production of nonferrous alloys carried on by the national metal div., Frankel Corp.

Amos A. Roberts, general sales and service manager, Baroid Sales div., National Lead Co., has been transferred from Tulsa to Houston.

John D. Ruschak is with the Dravo Corp., Pittsburgh.

George M. Lee has rejoined the staff of Ventures Ltd. and associated companies. He is in Uganda, British East Africa working on the development of metallurgical processes for Kilembe Mines Ltd.

Harry C. Cook recently became senior research engineer for the Air Reduction Co., research laboratories, Murray Hill, N. J.

Frederick R. Jeffrey is now manager of the ore dept., International Minerals & Metals Corp., and treasurer and assistant to the president, National Zinc Co., Inc., New York.

Edward L. Klopfer is now associated with the Gross Machinery Co., Inc., Kenmore, N. Y.

Charles Yaker has joined the scientific laboratory, Ford Motor Co., Dearborn, Mich.

G. O. John has taken a position in the plant investigation dept., Sulphide Corp. Pty. Ltd., Toronto, N.S.W., Australia.

A. E. Van Cleve, vice-president of Crucible Steel Co. of America has been appointed special assistant for mutual security matters to the under secretary of the army.

F. H. Dyke has been promoted to vice-president of U. S. Metals Refining Co. He will continue as general manager of the Carteret, N. J. plant.

Henry D. Mercer, president of States Marine Corp., New York has been named to the board of directors of Republic Steel Corp.

Louis E. Marchi, inorganic chemist in the ceramics and minerals research dept., Armour Research Foundation, has been promoted to senior chemist.

A. Taylor has been appointed project supervisor in the physics dept., Horizons, Inc., Cleveland. He had been head of the physics section, Mond Nickel Co., Ltd.

Louis Fernandez, group leader in the research dept., Monsanto Chemical Co., phosphate div., Anniston, Ala., has transferred to the division's technical sales dept., St. Louis.

Harry P. Davison was elected a director of the U. S. Steel Corp., and a member of the finance committee.

Willard J. Campbell was appointed sales manager of the Philadelphia div., Solar Steel Corp. **Sidney Taylor** has been made manager of the newly established sales office in Worcester, Mass.

M. Douglas Banus has been promoted to associate director of research in charge of chemical research laboratories, Metal Hydrides, Inc., Beverly, Mass. **Robert W. Bragdon** has been made assistant director of research. **Bernard A. Gruber** has joined the engineering staff.

Harold C. Erskine, manager of the Cleveland works of Aluminum Co. of America, has been named assistant division manager for die casting operations.

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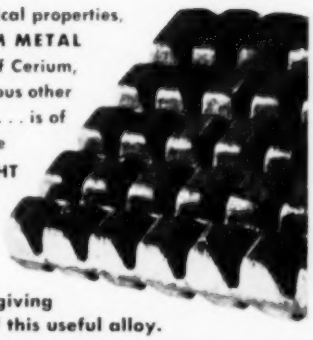

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MANGUM WEBB

Mangum Webb has been elected vice-president of Chemical Construction Corp.

Ernest Ohsol has been appointed manager of the new product development laboratory, General Electric Co., Pittsfield, Mass.

E. E. Ensign, formerly research metallurgist at the Ford Motor Co., has joined the Applied Research & Development Corp., New York, as vice-president.

John F. Schnur, foundry superintendent for the McLean Iron Works, Palatka, Fla., has been named foundry technologist at Armour Research Foundation of Illinois Institute of Technology. He will be assigned to the international div. in India.

A. A. Prier has been appointed sales manager of Solar Steel's new Nashville, Tenn. sales office.

S. Allen Oviatt has been made manager of sales engineering, Kentanium products, for Kennametal, Inc.

Jerome F. Ferdinand has been elected vice-president in charge of sales, Wales-Strippit Corp., North Tonawanda, N. Y.

Alfred H. Hesse has become vice-president and general manager of Steinac, Inc., Chicago, Ill. Mr. Hesse had been associated with R. Lavin & Sons, Inc., as metallurgist and advertising manager.

Robert F. Thomson has recently been named head of the dept. of metallurgy, General Motors Research Laboratories, Detroit.

Carl A. Meyer, Jr. has accepted a position as metallurgist in the quality control dept. of the Wheeling Steel Co., Weirton, W. Va.

Mars G. Fontana, professor and chairman, dept. of metallurgy, Ohio State University, has been elected president of the National Assn. of Corrosion Engineers.

Raymond J. Zale has been appointed sales metallurgist for the Firth Sterling Steel & Carbide Corp., Pittsburgh.

Obituaries

George E. Steudel (Member 1939) died on Jan. 16, 1952. Mr. Steudel was born at Chilton, Wis., in 1884 and graduated from the University of Wisconsin in 1911. After graduation he joined the Illinois Steel Co. as an experimental engineer. In 1913 he was made foreman for the first and two years later became blast furnace apprentice. In 1917 Mr. Steudel became assistant superintendent, I. E. blast furnaces. He was promoted to superintendent of blast furnaces at the Milwaukee works and in 1923 returned to the south works. For ten years he was assistant superintendent of the I. H. E. blast furnaces and in 1936 became division superintendent.

Bethune Glass Klugh (Member 1907) died in Birmingham, at the age of 71 years. He was born at Columbia, S. C., on Mar. 13, 1880. He entered the state university at Columbia. After two years he transferred to the University of North Carolina, taking a general scientific course with a chemistry major. He studied an extra year at the University of Washington, specializing in electro chemistry and mining.

In 1905 he entered the employ of the Toledo Furnace Co. as chief chemist and assistant manager. During this period he became interested in sintering iron bearing materials. Mr. Klugh joined the American Ore Reclamation Co. as chief engineer in 1910. He signed his first patent in 1910 for an agglomerating furnace for a sintering machine.

In 1917 Mr. Klugh transferred to the Southern Manganese Corp., the original unit of the Swann Chemical Co. which was purchased by Monsanto Chemical Co. in 1935. In 1919 he designed the first electric furnace to make phosphoric acid commercially. At the same time he compiled data on ferromanganese and prepared a complete report on the subject. He was credited with the early ferromanganese production of the Swann Co.

He returned to the American Ore Reclamation Co. in 1920 as chief engineer and manager, remaining until 1926 when he rejoined Swann. At American Ore he was credited with the responsibility for most of the early work in sintering and for the design and building of sintering plants.

When he returned to Swann in 1926, Mr. Klugh became a vice-president of the company. Here he continued his development work on phosphorus compounds and made an extensive survey of the phosphate rock fields in Tennessee and north Florida.

Mr. Klugh was the designer of the huge sintering machine at Columbia which is part of the largest elemental phosphorus plant in the world. In 1937 the company received the Chemical and Metallurgical Engineering Award based upon the contribution to the chemical industry brought about by the engineering achievement at Columbia. Mr. Klugh authored many technical papers and had approximately 30 patents.

At the time of his death Mr. Klugh was consultant to the company's phosphate div.

Alan Morris

An Appreciation by John L. Christie

Alan Morris, chief metallurgist of Bridgeport Brass Co. from 1933 to 1950, died on Mar. 18, 1952 in the Palmer Memorial Hospital, Boston. Dr. Morris had been in failing health for a year or more and he had gone to Boston for examination and treatment. His death was brought about by a sudden coronary occlusion.

Alan Morris was born in Salt Lake City on Nov. 26, 1890, the son of Frederick K. Morris, a mining engineer, and Emma Lang Morris. He was educated in New York City, where the family had moved, and he graduated from high school in 1906. After working for 10 years to earn enough money he entered Columbia in 1919 and he graduated in 1923 with degrees of B.A., B.S., and metallurgical engineer. At Columbia he came under the influence of Prof. William Campbell and Prof. Colin Fink. He became a member of Alpha Delta Phi. He rowed on the Columbia varsity crew. He was elected to Phi Beta Kappa and Tau Beta Pi. In 1938 he received the degree of Doctor of Engineering from Yale University which he attended in his spare time.

On enlisting in May 1917, Morris went to Officers' Training Camp at Fort Monroe, and as First Lieutenant went to France in September. He served with French troops and later with the 32nd Div. Heavy Artillery. He was promoted to Captain and was cited for bravery under fire near Verdun.

On graduating from Columbia Morris joined Bridgeport Brass Co. as a sales engineer. He transferred to the metallurgical dept. and became successively chief metallurgist, director of research, and metallurgical consultant.

Morris, by his sound training, keen mind, clear thinking, and broad knowledge, won the respect of fellow workers and management alike. His interests covered such diverse fields as manufacturing methods and processes, metal properties, corrosion resistance, and new alloy development. Under his direction the company's research and metallurgical dept. expanded in size and scope.

Morris was the author of several

technical papers and articles covering a wide range of subjects. He was the holder of several patents. In addition to the AIME he was a member of ASTM, ASM, ASME, AWS, Institute of Metallurgy (British), Copper & Brass Research Assn., and API.

Morris in 1927 married Marion Tuttle of Bridgeport who survives. They were inseparable. Their home is in Nichols, a suburb of Bridgeport, where they lived quietly and enjoyed the nicer things of life.

Professor Frederick K. Morris of Montgomery, Ala., is a brother.

Alan Morris will be remembered by his friends for his cheerfulness, gentleness and kindliness, and his devotion to his wife and to his work.

Edward G. Mahin

An Appreciation by
J. E. Drapeau, Jr.

Prof. Edward G. Mahin's death leaves an empty chair in university and engineering circles.

Prof. Mahin was born at Lafayette, Ind., on Aug. 16, 1876, son of Chas. W. and Mary Ogden Mahin. Dr. Mahin received his B.S. degree at Purdue University in 1901. At Johns Hopkins University he was awarded an M.S. degree and Ph. D. degree. He was elected to Phi Beta Kappa, Sigma Xi, Tau Beta Pi, and Phi Lambda Upsilon. Dr. Mahin started teaching at Purdue in 1901. He was a full professor from 1914 to 1925.

In 1925 Prof. Mahin left Purdue to join the staff of Notre Dame where he organized the dept. of metallurgy. In 1932, he was head of the metallurgy dept. which he retained until his recent retirement in 1949. He served on the Graduate committee, which he helped form in the late 1920's.

His activities were not confined to the universities. He worked at the U. S. Naval Engineering Experimental Station in 1917-18 and Michigan Smelting & Refining Co. in 1919 during the summer.

He was author of numerous technical articles and books such as *Quantitative Analysis, Introduction to Quantitative Analysis, Quantitative Agriculture Analysis, Elementary Physical Metallurgy* and the International Chemical Series text books.

He achieved the honor of being president of the Indiana Academy of Science in 1928 and was a past trustee of the American Society for Metals. Notre Dame awarded him the Distinguished Teacher award.

Dr. Mahin was an active member of our AIME, ASM, Iron and Steel Institute, British Institute of Metals, Academy of Science, American Foundrymen's Assn., Institute of Aeronautical Sciences and the Round Table Club.

His counsel and advice were freely given to literally thousands of students and engineering concerns throughout the nation. AIME extends their condolences to Dr. Mahin's family.

Dr. Mahin leaves a son, William E. Mahin, who is outstanding in engineering circles, a past chairman of Chicago Section of ASM and present chairman of the Chicago Section of our AIME.

John G. Munson (Member 1947), former vice-president, raw materials, U. S. Steel Corp. of Delaware, now merged with U. S. Steel Co., died on Mar. 29, after a long illness. Mr. Munson was 67 years old, and had served 31 years with the U. S. Steel organization, prior to his retirement on Dec. 31, 1950. He was born in Bellefonte, Pa. in 1885 and graduated from Yale University (B.S.) in 1905. Following graduation he joined the N. Y. Continental Jewell Filtration Co., as a rodman on tunnel construction in Washington, D. C. From 1906 to 1908 he served as superintendent on various construction projects in New Haven, Conn. and Baltimore, Md. In 1909 he was associated with the J. G. White Engineering Corp. as construction superintendent. During his employment with that company he had charge of the construction of the Ocoee developments of the Tennessee Power Co. During World War I he was in charge of nitrite plant construction at Sheffield, Ala. In 1919 Mr. Munson joined the Michigan Limestone & Chemical Co. and Bradley Transportation Co. He became president and director of both companies in 1925. He was elected vice-president, raw materials of the former U. S. Steel Corp. of Delaware in 1939.

NECROLOGY

Date Elected	Name	Date of Death
1922	Robert C. Coffey	January, 1952
1941	N. L. Davis	Mar. 2, 1952
1920	H. W. Gould	Nov. 14, 1951
1944	John G. Green	July, 1951
1940	Thomas J. Hamilton	October, 1951
1929	M. D. Hasbrough	Mar. 19, 1952
1920	Joseph Robert Lillard	Feb. 19, 1952
1920	Edward G. Mahin	Feb. 4, 1952
1923	Alan Morris	Mar. 15, 1952
1947	John G. Munson	Mar. 29, 1952
1936	Stuart W. Norton	Unknown
1903	Ambrose E. Reig	Feb. 29, 1952
1941	Ellsworth B. Shreve	Aug. 12, 1951
1942	Walter W. Stegman	July 30, 1951
1946	C. C. Van Deventer	May 18, 1951
1939	A. L. Weil	Unknown
1901	Charles Henry White	Mar. 17, 1952

Proposed for Membership
— Metals Branch AIME —

Final AIME membership on Feb. 29, 1952 was 17,221, in addition 2741 Student Associate were enrolled.

ADMISSIONS COMMITTEE

F. D. Josey, Chairman, Thomas G. Mayo, Vice-Chairman, Harold S. Bell, F. W. Boubel, R. H. Chenhall, T. W. Nelson, J. B. Neuffer, John T. Sherman, A. C. Hoover, Dean Harvey, C. A. R. Lansing II, G. P. Larrick, F. A. Nichols, and C. Lapsley Reed, Jr.

The Institute desires to extend its professional services to those who can be of material and direct aid during an emergency, and does not desire as members persons who are unqualified. Particular attention is urged to insure that no man of prominence, and immediately in advance, the Metallurgical office of scores of people, are found who are known to be unqualified for AIME membership.

In the following list C/S means election of status; R, reinstatement; M, Member; J, Junior Member; A, Associate Member; S, Student Associate.

Alabama

Birmingham—Worthington, Bobbie W. (M)

California

Berkeley—Robinson, Allen T. (A); (C.S.-S.A.)
Burbank—Lambers, Albert V., Jr. (M); (R. C.S.-J.M.)
Glendale—Davis, George C., Jr. (A)
San Jose—Austin, Leslie W. (M)
San Jose—Minefield, John D. (A)

Colorado

Leadville—Doctor, William R. (M)

Connecticut

Greenwich—Diehl, Richard C. (M)
Stamford—Vanderpool, Jean (M)
Torrington—Purdon, Donald E., Jr.
Wethersfield—Post, John H., Jr.

Illinois

Evanston—Hayden, Carl F. (M)
Forest Park—Cooper, Peter F., Jr. (J)
Lemont—Drake, Joseph R., Jr. (C.S.-S.J.)
Lemont—Sowder, Sidney P. (M); (R.C.S.-J.M.)
Park Forest—Lumsdaine, Lewis B., Jr. (M); (C.S.-A.M.)

Indiana

Munster—Christopher, Charles E. (M)
Munster—Esposito, Charles W. (M)
Notre Dame—DeMoss, John F. (M); (C.S.-A.M.)

Massachusetts

Cambridge—Gregoire, Eric (J); (R.J.)

Michigan

Berrien—Pearson, Dalton A., Jr.
Manistique—MacNeil, Samuel G. (M)

Montana

Butte—Anson, Sheikh M. (J)

New Jersey

New Brunswick—Schlegel, William L. (A)
West Orange—Ziegler, George N. (J)

New York

Bethpage—Janson, Ernest C., Jr. (A)
Garden City—Dorrington, Tore O. (M)
Huntington, L. I.—Preston, John (J)
West Goshen—Frank, Ernest L. (A)
Yonkers—Fiori, Palmer R. (A)
Yorktown—Sherwood, Robert C. (M)

Colorado

Leadville—Doctor, William R. (M)

Connecticut

Greenwich—Diehl, Richard C. (M)
Stamford—Vanderpool, Jean (M)
Torrington—Purdon, Donald E., Jr.
Wethersfield—Post, John H., Jr.

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Garden City—Dorrington, Tore O. (M)
Huntington, L. I.—Preston, John (J)
West Goshen—Frank, Ernest L. (A)

Ohio

Cleveland—Kopczewski, Henry (J)
Cleveland—Sherif, Samuel K. (J)
Lakewood—Clapp, Francis J. (J)
Lakewood—Johnson, Fred W. (M)
Springfield—Lorraine, Boyd O. (M)
Wapakoneta—Heiser, Hans J. (M); (R.C.S.-J.M.)

Pennsylvania

Bethlehem—Foster, James C. (M)
Pittsburgh—Fratini, Raymond V., Jr. (J); (C.S.-S.J.)
Pittsburgh—Brubaker, Walter B. (M)
Portsmouth—Weir, Frank (M)

Tennessee

Kingsport—Stansbury, Eby E. (M); (C.S.-A.M.)
Maryville—Vanderbeeden, Eugene T. (J); (C.S.-S.J.)

Texas

Houston—Petersen, Robert L. (A)

Utah

Salt Lake City—Hatfield, Dorcil W. (M)

Washington

Tacoma—McGrath, Kenneth W. (J); (R.C.S.-S.J.)
Tacoma—Lee, Hsin-Te (A); (C.S.-S.A.)

West Virginia

Glen Ferris—Magruder, William H. (J); (C.S.-S.J.)

Canada

Montreal—Lavigne, Maurice J. (M); (C.S.-A.M.)
Toronto—Strzeszek, William (C.S.-S.J.)
Valcartier, P. Q.—Brochet, Jean M. (M)
Toronto—Goldcamp, Clarence W. (M)

England

Birmingham—Bignell, Harold W. G. (M)

Coming Events

May 1-3. American Foundrymen's Society, Centennial Foundry Congress and Show, Convention Hall, Atlantic City, N. J.

May 1-3. National Welding Supply Assn., fall convention, Chicago.

May 1-6. Electrochemical Society, Inc., spring meeting, Benjamin Franklin Hotel, Philadelphia.

May 2-6. National Air Pollution Symposium, Huntington Hotel, Pasadena, Calif.

May 5-9. Scientific Apparatus Makers Assn., annual meeting, Edgewater Beach Hotel, Chicago.

May 6-9. National Electrical Mfrs. Assn., 25th electrical-lighting exposition and conference, Cleveland.

May 9-10. AIME, joint meeting, Industrial Minerals Div. and Metals Branch, Davenport Hotel, Spokane, Wash.

May 11-14. American Institute of Chemical Engineers, Atlanta Biltmore, Atlanta.

May 11-14. Industrial Furnace Mfrs. Assn., annual meeting, Homestead, Hot Springs, Va.

May 14-16. Society for Experimental Stress Analysis, spring meeting, Hotel Lincoln, Indianapolis.

May 15. AIME, Cleveland Section, subject: Metallurgy Bldg., Case Institute of Technology, Cleveland.

May 17. AIME, Chicago Section, President's night dinner dance, Sherman Hotel, Chicago.

May 19-21. American Supply & Machinery Mfrs. Assn., annual convention and conference, Inverness Country Club, Tampa, Fla.

May 22-24. American Society for Quality Control, annual convention, Onondaga County War Memorial, Syracuse, N. Y.

June 2-4. Chemical Institute of Canada, annual conference, Montreal.

June 4-14. Mechanical Handling Exhibition and Convention, Olympia, England.

June 6. AIME, Columbia Section, dinner meeting, Spokane Hotel, Spokane, Wash.

June 16-20. Industrial Finishing Exposition, International Amphitheatre, Chicago.

June 23-27. ASTM, 55th anniversary meeting, Hotel Statler, New York.

July 1-Sept. 30. Centennial of Engineering, Chicago.

Aug. 25-29. Oak Ridge Summer Symposium, Oak Ridge, Tenn.

Sept. 3-6. AIME, fall meeting, Palmer House, Chicago.

Sept. 3-6. AIME Industrial Minerals Div., annual fall regional meeting, Chicago.

Sept. 3-13. AIME, Chicago Section, Centennial of Engineering, Chicago.

Sept. 10-12. Porcelain Enamel Institute, annual shop practice forum, University of Illinois, Palmer House, Chicago.

Sept. 11-13. American Institute of Chemical Engineers, Palmer House, Chicago.

Sept. 22-25. American Mining Congress, Metal and Nonmetallic Mining Convention and Exposition, public auditorium, Denver.

Sept. 23-25. Institution of Mining and Metallurgy, conference on mineral dressing, Royal School of Mines, London.

Oct. 3. AIME, Southern Ohio Section, National Open Hearth Steel Committee, Deshler-Wallick Hotel, Columbus, Ohio.

Oct. 10. AIME, Eastern Section, National Open Hearth Steel Committee, Warwick Hotel, Philadelphia.

Oct. 10. AIME, Southwestern Section, National Open Hearth Steel Committee, Peoria, Ill.

Oct. 20-22. AIME, Institute of Metals Division meeting with National Metal Congress, Hotel Adelphia, Philadelphia.

Oct. 22-24. Porcelain Enamel Institute, Greenbrier Hotel, White Sulphur Springs, W. Va.

Oct. 28. Assn. of Consulting Chemists & Chemical Engineers, Inc., annual symposium, Hotel Belmont Plaza, New York.

Nov. 3. AIME, Pittsburgh Section, National Open Hearth Steel Committee, Hotel William Penn, Pittsburgh.

Dec. 1-6. AIME, Electric Furnace Steel Conference, Hotel William Penn, Pittsburgh.

Dec. 7-10. American Institute of Chemical Engineers, Cleveland and Carter Hotels, Cleveland.

Dec. 8. AIME, Arizona Section, all day meeting, Tucson.

Feb. 16-19, 1953. AIME, annual meeting, Statler Hotel, Los Angeles.

Apr. 20-22. AIME, National Open Hearth and Blast Furnace, Coke Oven, and Raw Materials Conference, Hotel Statler, Buffalo.

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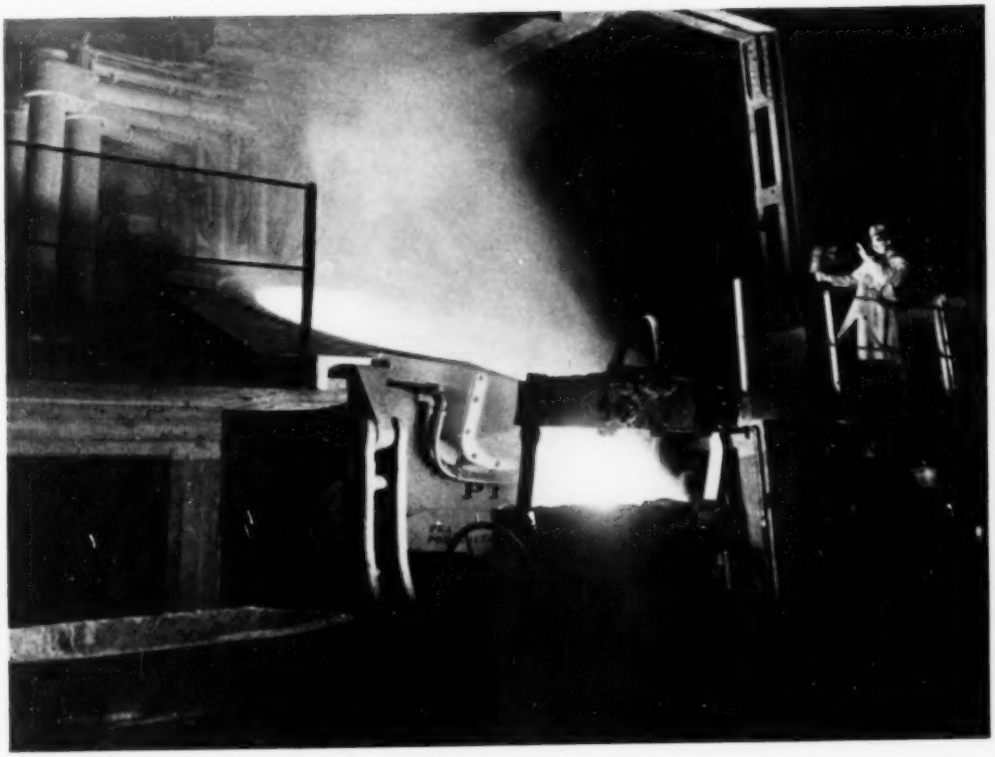

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